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Review

Use of Clay and Titanium Dioxide Nanoparticles in Mortar and Concrete—A State-of-the-Art Analysis

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Abstract: In the past decades, nanomaterials have become one of the focal points in civil engineering research. When added to cement-based construction materials (e.g., concrete), it results in significant improvements in their strength and other important properties. However, the final mix characteristics depend on many variables that must be taken into account. As such, there is no general consensus regarding the influence upon the original material of certain nano-sized additives, the optimum dosage or the synergistic effect of two or more nano-materials. This is also the case for titanium dioxide (TiO_2) and nanoclay (NC). The paper focuses on reporting the existing research data on the use of the above-mentioned materials when added to mortar and concrete. The collected data is summarized and presented in terms of strength and durability properties of cement mortar and concrete containing either TiO_2 or NC. Both nano-materials have been proven, by various studies, to increase the strength of the composite, at both room and elevated temperature, when added by themselves in 0.5%~12% for TiO_2 and 0.25%~6% for NC. It can be inferred that a combination of the two with the cementitious matrix can be beneficial and may lead to obtaining a new material with improved strength, elastic and durability properties that can be applied in the construction industry, with implications at the economic, social and environmental levels.

Keywords: nanomaterials; nanoclay; titanium dioxide; cementitious material; sustainability

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1. Introduction

Various global-sized revolutions have changed previously held ideas, encouraging both research and industry. Nowadays, the growth and general evolution within societies is significantly accelerated by technological breakthroughs. This has resulted in new problems which are currently unsolved, namely pollution and the threat of natural resource depletion. In the field of civil engineering, researchers are compelled to mitigate the influence the construction industry has, considering that in 2020 it was responsible for approximately 37% of the global process-related carbon dioxide emissions. Of this percentage, 10% was generated by the manufacturing processes of building materials [1]. Nanotechnology has influenced almost all of nowadays advancements in terms of mechanical properties and durability of materials, construction materials included. The term "nanomaterial" has been defined by the European Union Commission [2] in the Official Journal of the European Union as being an artificially-created or a natural material, of which at least 50% of the particles have one, or more, external dimensions between 1 nm and 100 nm. In cementitious composites, many components fit this description, and their study is now possible due to the progress of material characterization techniques at this level.

To this day, several nanomaterials have been studied with respect to their applications in the construction industry. In addition to strength, other properties were also considered within the framework of nanotechnology. A recent study [3] highlighted the positive

effect of several nanomaterials on the thermal resistance of cementitious composites, of which nano-silica stands out as being one the most studied materials. Additionally, several other nanomaterials were mentioned as increasing the high-temperature strength of the cement-based composites: carbon-based nanomaterials (carbon nanotubes, carbon nanofibers, graphene oxide, graphene nanoplatelets), nanoclay, nano-alumina, nano-iron oxides and nano-titania. Other studies [4,5] focused on the environmental impact of using nanoparticles in concrete, concluding that TiO_2 has a positive influence from this perspective [4].

The present work aims at creating a structured report encompassing the existing information about the impact of titanium dioxide (TiO_2) and nanoclay (NC) on cementitious composites from the point of view of strength enhancements and improvement of durability characteristics. A definite remark upon the influence of nanoclay on cement mortar or concrete is difficult to advance, as the variables change from one study to another. An important change is the type of nanoclay used in the study, the number of curing days or the additives introduced in the mix, e.g., fly ash, polypropylene fibers, superplasticizer, silica fume. These influence the final measured values for the strengths of the composite. Titanium dioxide nanoparticles succeed in improving both mechanical properties and photocatalytic reactions of cement mortar and concrete due to their chemical and physical properties. They are usually used in mortar/concrete mixes combined with superplasticizers in order to obtain a higher workability. Considering that TiO_2 is a non-reactive powder, there are studies in which pozzolans were added with the purpose of promoting the cement hydration reaction, e.g., fly ash, silica fume.

The mechanisms of improving the strength and durability properties of cementitious materials by using each of the two nanomaterials are different from one another but the end results are similar: NC is a highly pozzolanic material with significant influences on strength and durability at later ages while TiO_2 is inert and plays a filler effect. However, due to the very small particle sizes of nano-TiO_2, it serves as nucleation sites in the cement matrix with benefits in terms of strength and durability at earlier ages compared to NC. The information summarized in this work could serve as the starting point for future research works investigating the influence of combining TiO_2 and NC on the strength, elastic and durability properties of cement mortar and concrete.

2. The Influence of Nanoclay on Cementitious Materials

The use of nanoclay as a component of other materials started in the late 20th century when researchers observed that, by using this nanomaterial, the properties of the new composite material improved as compared to the material without the addition of nanoclay [6–9]. Among its first applications were the polymer matrices. The next observable research stage involved combining nanoclays with other materials of the same size (e.g., carbon nano-tubes [10,11]) as well as using them in cementitious mixes [12–14].

Nanoclay is defined as a layered mineral silicate, which, due to its filler and pozzolanic characteristics, succeeds in enhancing the mechanical and durability properties of several types of materials such as polymers or cement-based materials [15–18]. The use of such layered crystals, i.e., clays, in polymer composites resulted in improved physical properties and in the heat deflection temperature mainly due to their high surface area [19]. Moreover, the benefits of using nanoclay did not go unnoticed and their field of application soon extended to construction materials.

2.1. Types of Nanoclay Used in Combination with Cementitious Materials

There are several types of natural clays that were used as raw materials for the manufacturing of nanoclays: bentonite, montmorillonite, kaolin, illite, halloysite. They all have the same base crystalline structure, with the difference coming from the types of bonds between the stacked layers. This leads to different properties with direct effect in terms of the obtained results when added in the composition of another material [20,21]. Most of the research in terms of nanoclays used in cement-based materials is conducted with

montmorillonite or kaolin clays, usually in a modified form, in order to obtain a significant improvement of the physical properties of the resulting material.

Montmorillonite (MMT) nanoclay has a 2:1 layer structure and very weak Van der Waals forces keeping the outer layers together. This means that when combined with water the particles absorb water molecules and the distance between layers increases, leading to swelling [21]. A more detailed explanation of this phenomenon was given in [20]. Based on the available information at that time, one way to decrease the swelling was to add exchangeable cations with a lower hydration energy, thus obtaining a more hydrophobic nano-montmorillonite. Some researchers based their studies on this method and used ammonium cations to decrease the hydrophilicity of MMT obtaining an organo-modified montmorillonite [12,17,22–27]. Other studies prepared the nanoclay particles by subjecting them to very high temperatures, in the range of 750–900 °C for 2 h, obtaining a nano-calcined montmorillonite clay [28–31].

Unlike montmorillonite clays, kaolin ones have hydrophobic properties, as they are composed only of two layers connected not only by Van der Waals forces but also by hydrogen bonds which do not allow water molecules to enter between them [21]. Therefore, no additional treatment is needed before using nano-kaolin particles in the cement-based composites. However, when subjected to high temperatures, due to the calcination process, the hardness of the kaolin clay nano-particles is increased together with their degree of pozzolanicity. The particles change their shape and size, become more hydrophobic, as in the case of MMT nanoclay, and increase their whiteness. Due to its improved afore mentioned properties, the calcined kaolin nanoclay, i.e., metakaolin, became the focus for researchers instead of the raw kaolin nanoclay [32–36].

2.2. Chemical Structure and Properties

Nanoclay is a general term for the nanoparticles, which, as mentioned above, are comprised of layered mineral silicates [37] and, depending on the arrangement of the layers in the crystal lattice and the existing types of bonds, they result in different types. As mentioned before, MMT and kaolin are the most used types of nanoclays in civil engineering. Kaolin is a 1:1- type of clay mineral consisting of one silica tetrahedral sheet connected to the alumina octahedral sheet by means of the hydrogen atoms, having the chemical formula $Al_2Si_2O_5(OH)_4$ [38]. Montmorillonite, on the other hand, is a 2:1-type of clay mineral having a sandwich-like structure and it consists of two silica tetrahedral sheets with a single alumina or magnesium octahedral sheet in between, having the formula $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$ [17,39]. The dimension of a phyllosilicate sheet is approximately 1 nm, whereas the nanoparticle size is in the interval 30–100 nm [40].

The benefits of using them in combination with cement are two-fold. On one hand, their very small particle size leads to a higher specific surface area than the micro-sized particles, on which the hydration products can form. Moreover, because of this, nanoclay particles succeed in entering the existing voids between the cement paste and the aggregates, at a nanoscale level, thus obtaining a decrease in porosity. Combining the aforementioned phenomena occurring inside the cement-based material, the resulted strength and durability increases [18,37]. On the other hand, the increase in strength is given also by the nanoclay chemical reactivity with calcium hydroxide (CH) during the hydration process. Having in its composition two layers of silica, nanoclay promotes the formation of calcium-silicate-hydrates (CSH) in a pozzolanic reaction. The increase in the concentration of CSH leads to an increased strength of the material [14,41].

2.3. Nanoclay Particles in Cementitious Materials—Technological Flow

Because of their very small size, nanoclay particles behave differently when mixed with water than the micro- or macro-sized particles usually used in civil engineering. The effect of electrostatic attraction is greater in case of nanoparticles leading to the occurrence of flocs. When water is added, the flocculation effect can become more prominent, especially in case of MMT clays, where the water molecules can intercalate with the outer layers of

the crystal and cause swelling [21,42]. This agglomeration of particles within the mortar or concrete has a negative impact upon the strength. Therefore, there is a stringent need for particle dispersion before the start of cement hydration.

The scientific literature gives two main ways in which this dispersion can be performed. The first one, which is the most recommended one, is to introduce the nanoclay particles in the water and then to subject the solution to ultrasonic waves. In this manner, the vibration caused within the molecules due to the impact of ultrasonic waves will prevent nanoclay particles to flocculate and will disperse them. Then the nanoclay-water solution can be used in two different ways to create the mortar or concrete samples: mechanical mixing or ultrasonic mixing. The mechanical mixing follows the steps given in ASTM C305 norm [18,43]. Using the ultrasonic mixing, the dry mixed materials (cement, sand, additives) are added to the nanoclay suspension already obtained and the ultrasonication is started again for the whole mix [44]. A previous study [45] concluded that in case of nanoclay, the sonication process has a positive effect on the final mechanical properties of the concrete samples. They also stated that the maximum allowable percentage of nanoclay used in cement-based materials is 5% [22,45].

The second method of dispersion is a simpler one and does not require any additional equipment than the one needed for preparing the mortar/concrete, namely, the dry mixing method. In this case, the mixing is performed in steps. The cement and the additives are dry mixed together with the nanoclay particles. In this manner, the nanoclay particles can be easily dispersed, due to the lack of a solving agent. Because the quantity of nanoclay is very small compared to that of cement, the distance between the nanoclay particles tends to increase during the dry mixing. This leads to a decrease in the flocculation probability when adding water. Afterwards, the aggregates are added and the mixing is restarted. Finally, the water is introduced in the composite [29,46].

A comparison between the previously mentioned methods of mixing nanoclay with cement-based materials, i.e., ultrasonication and dry mixing, showed that for a substitution of cement of 1–3% nanoclay, no differences were registered in terms of mechanical strengths. It was therefore concluded that both methods were equally reliable in properly dispersing nanoclay particles within the cement matrix [42].

2.4. Results of Laboratory Analyses (Microstructural Analyses)

When analyzing the nanoclay-cement-based material composite, the laboratory results vary depending on several factors, e.g., the nanoclay particle size, the nanoclay/cement ratio, the type of cement, the water/cement ratio, type and quantity of additives, type and size of aggregates. However, there are some common properties which are further discussed in this paper. Taking into account that when using sand or gravel, an important quantity of silica is introduced in the composite and the properties change significantly. The analyses will be presented considering this factor.

2.4.1. Scanning Electron Microscopy (SEM) Analysis

The layered structure of the organo-modified montmorillonite nanoclay (OMMT), obtained by cation exchange with quaternary ammonium cations, was extensively studied by means of SEM analysis [22]. Because MMT has a very high hydrophilicity, when it is introduced in the cement matrix, it begins to absorb the water from the cement matrix. In this manner, at first, the hydration of cement particles is slowed down and the workability is significantly reduced. The advantage of montmorillonite particles is that they begin to release the accumulated water at a later period during the hydration process of cement, leading to an improvement in strength. The phenomenon was later observed in other supplementary cementitious materials, such as zeolites, and it is now known as internal curing. However, the major problem with MMT particles, from this point of view, is that because of the initial occurring phenomenon, they introduce a water to cement ratio gradient near them as the quantity of water increases in that area. By increasing the water, the porosity is automatically increased, reducing the cohesion between the cement matrix

and MMT particles [17]. When adding OMMT instead of MMT the water/cement ratio gradient around the nanoclay particles is decreased and the development of cracks is hindered [17].

The effects of high temperatures on mortar containing 5 wt% nano-calcinated montmorillonite clay (NCMC) was also studied [28] by firstly analyzing the SEM images, presented in Figure 1, for samples with and without NCMC at 25 °C, 250 °C and 900 °C, at 28 days of curing. The investigations highlighted the positive effect the NCMC has on the mortar matrix, especially at the level of the interfacial transition zone (ITZ) between the aggregates and the cement paste (#2 in Figure 1d). It was therefore concluded that by adding NCMC to the mortar, a denser matrix was obtained [28] mainly due to the filler effect of the nanoparticles. Additionally, an increase in the pozzolanic activity was detected. When the temperature was increased to 250 °C, the cement hydration was accelerated and more CSH were obtained in case of NCMC mortar than in case of control mortar (#3 in Figure 1b,e) [28]. After 300 °C, the development of microcracks began and at 450 °C the cracks widened and were clearly visible as Portlandite started to degrade and CSH particles lost their structural integrity [47]. At 900 °C, wide cracks were present in the control sample (#4 in Figure 1c) leading to a significant strength loss. However, when adding NCMC in the mix, the cement matrix experienced fewer cracks (#4 in Figure 1f), thus leading to higher strength values [28].

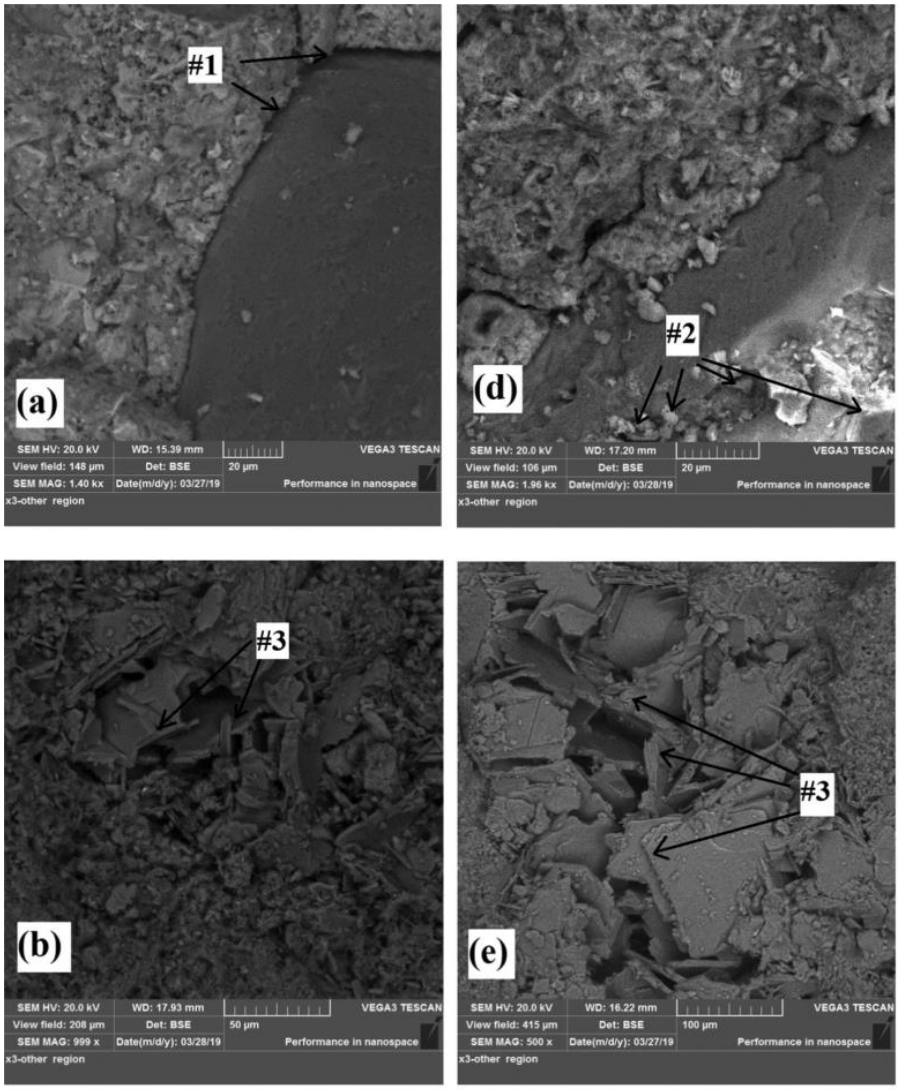


Figure 1. *Cont.*

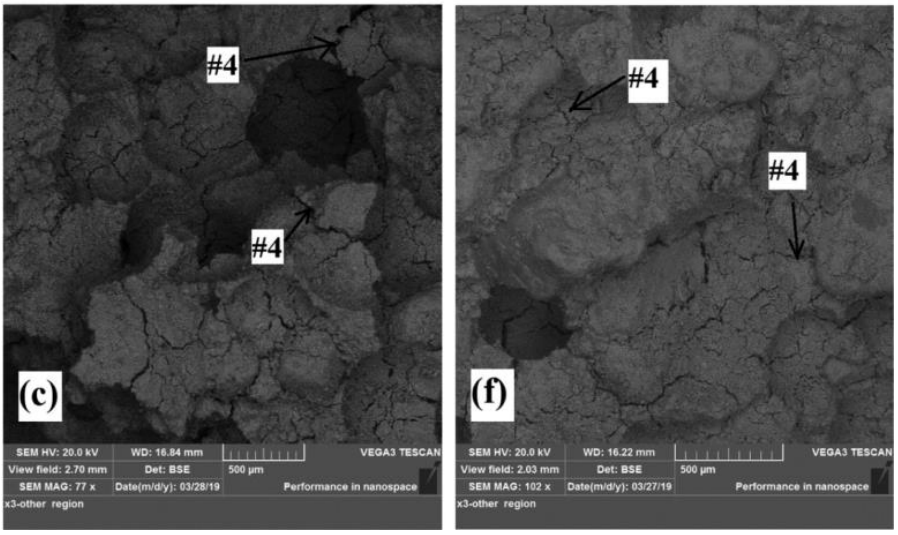


Figure 1. SEM images of fracture surfaces of control and modified mortar [28] (Reprinted/adapted with permission from Ref. [28]. Copyright 2018, ELSEVIER); (**a**) control at 25 °C, (**b**) control at 250 °C, (**c**) control at 900 °C, (**d**) NCMC mortar at 25 °C, (**e**) NCMC mortar at 250 °C, (**f**) NCMC mortar at 900 °C.

2.4.2. Thermogravimetric Analysis (TGA)

TG analysis is used to evaluate the influence of the temperature upon the considered material. Usually, the TGAs are conducted on cement paste samples because the aggregates significantly influence the final result. Generally, aggregates do not vary in weight when subjected to an increase in temperature so including them in the very small samples needed to run TG analysis would only lead to erroneous results [48,49].

Natural hydrophilic montmorillonite in 1% and 2% cement replacement was used to investigate the influence of temperature on the obtained cement paste. The heating rate for the TGA in this test was 30 °C/min. The study revealed that there were two main stages in the weight loss of cement paste: the dehydration of C-S-H at 105 °C and the CH decomposition at 470 °C [18]. The obtained results were in good agreement with the ones previously reported in general study on cement pastes [48]. At approximately 750 °C a third stage could be distinguished, corresponding to the decarbonation of calcium carbonate $CaCO_3$ [48]. It was shown that, as the percentage of nanoclay increases, the weight loss increases, indicating the property of natural montmorillonite to attract water molecules. Therefore, when heated, the samples began releasing the physically bounded water, its quantity being greater in case of samples with MMT compared to the control sample.

In contrast to the results presented in [18], the use of calcined natural montmorillonite clay resulted in a smaller weight loss compared to the control sample [28]. The stages of weight loss depending on the temperature were similar with the ones reported in [18]. However, during the first stage, i.e., 100–110 °C, there was no abrupt change in weight for the NCMC but a more gradual one due to the fact that the NCMC water absorption capacity has been significantly reduced by means of calcination. Between 430 °C and 470 °C the dehydration of weakly bound water from CH and CSH products occurred, followed by a reduction in weight between 580 and 680 °C when the strongly bound water was lost.

Similar results to the ones reported in [28] regarding the nano-calcined montmorillonite clay (CNCC) for 1, 2 and 3 wt% cement replacement were previously reported [29]. The earlier research work continued the study further on, including in the TG analysis samples of 1 wt% cement replacement by nanoclay modified with quaternary ammonium salt (NCC). It was observed that a smaller weight loss occurred when adding CNCC of 1 and 2 wt% than when using 1 wt% NCC. This result proved that nano-montmorillonite calcination has a greater impact on the decreasing the hydrophilicity than adding ammonium cations.

2.4.3. X-ray Power Diffraction (XRD) Analysis

When creating a new composite material, it is very important to know the influence that each component has upon the final result. In this regard, XRD analysis provides an insight regarding the mineralogical changes that occur inside the material, e.g., mortar/concrete, when adding nanomaterials, e.g., nanoclay [50]. Using 2 wt% nanoclay, untreated hydrophilic montmorillonite by weight of cement replacement and subjecting the samples to 25 °C, 200 °C, 400 °C and 600 °C, it was observed that the intensity of CSH is higher for all samples combined with NC, as shown in Figure 2, by comparison with the control samples, which leads to an increase in strength [18]. The increase in CSH crystals quantity became more prominent when increasing the temperature. Thus, for samples subjected to 400 °C and 600 °C, there was a strong peak for the CSH crystals (at 2θ = 28°), while up to 400 °C, the quantity was significantly smaller. Moreover, the intensity of CH (2θ = 18°) decreased with the temperature, as the cement hydration accelerated [18].

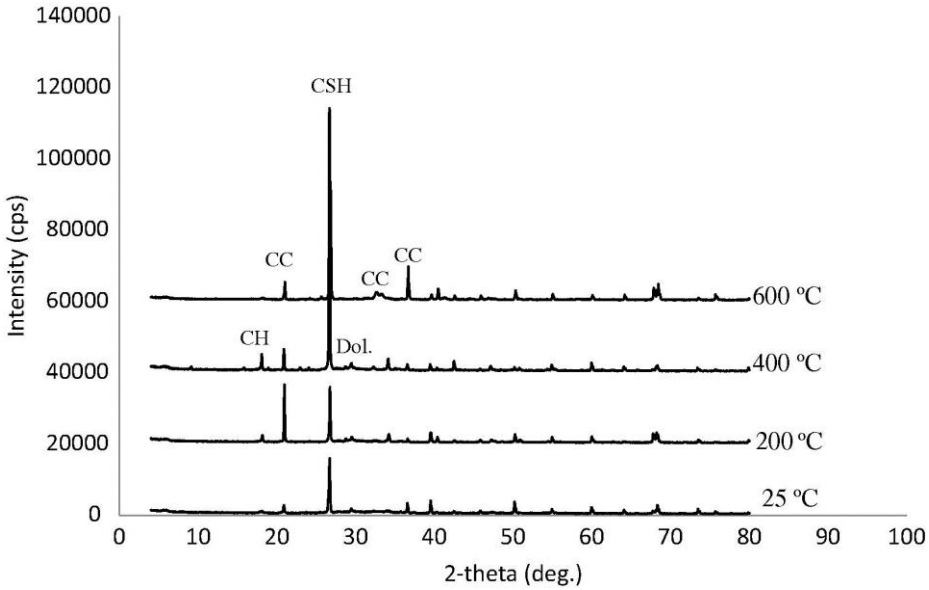


Figure 2. XRD patterns of mortar with 2% untreated hydrophilic montmorillonite nanoclay after exposure to different temperatures [18] (Reprinted/adapted with permission from Ref. [18]. Copyright 2020, ELSEVIER).

In another study, XRD analysis was performed on mortars combined with nano-calcined montmorillonite clay CNC, which lead to the conclusion that the calcined nanoclay had a positive effect upon the strength of the material, as it promoted the consumption of CH crystals and the formation of CSH gel [28]. The researchers used a 5 wt% nanoclay cement replacement and the analyzed samples were previously subjected to temperatures of 25 °C, 150 °C and 900 °C. The authors interpreted the presence of belite in the composite as an indicator for the level of both CH and CSH decomposition. Based on this remark, it can be stated that calcined nano-montmorillonite clay has a positive effect on the material properties, even at elevated temperatures as high as 900 °C. At that temperature, the control sample exhibited an important increase in belite, i.e., 8% higher than nanoclay mortar [28].

Similar results have been previously reported in a study in which the cement was replaced with 1, 2 and 3 wt% CNC and observed a reduction in the CH quantity (approximately 28% compared with control sample) [29]. This was attributed to the pozzolanic reaction which consumed the CH and led to the formation of CSH gel. Moreover, the increasing in the unreacted dicalcium silicate (C_2S) and tricalcium silicate (C_3S), compared with quantities from the control cement paste, confirmed the pozzolanic property of CNC. However, as the percentage of nanoclay introduced in the cement was increased, the reduction of CH crystals decreased. Moreover, a smaller quantity of C_2S and C_3S was obtained

for 3 wt% CNC than for 1 wt% CNC, indicating a decrease in the pozzolanic activity. The XRD patterns for 1% CNC and the ones obtained for 1% cement replacement with montmorillonite nanoclay indicated that the calcined nanoclay led to a higher pozzolanic activity than the organo-modified nanoclay [29].

2.5. Material Strength Improvements

A definite remark upon the influence of nanoclay on cement mortar or concrete is difficult to advance, as the variables from one study to another are changing. An important change is the type of nanoclay used in the study, the number of curing days or the additives introduced in the mix, e.g., fly ash, polypropylene fibers, superplasticizer, silica fume. These influence the final measured values for the strengths of the composite. However, considering the reports from recent studies, the use of nano materials, nanoclay included, results in a denser microstructure of the material with net benefits in terms of strength and durability properties [51–53]. From this perspective, the current paper presents the literature results in a centralized manner identifying the possible influences on the reported results, where they are present. Moreover, the paper extracts from the literature only the results for the cement-based composites, where the main cement replacement material is nanoclay.

2.5.1. Splitting Tensile Strength

Taking into account that concrete/cement mortar elements have a very poor tensile strength and that their main strength develops under compression, the number of studies analyzing the tensile strength for a simple combination of cement-based material and nanoclay is very limited. However, based on the information presented in Sections 2.2 and 2.4 regarding the influence of nanoclay on the chemical and physical properties of the cement composite, an improvement in the tensile strength is expected. The porosity decrease, the prolonged hydration and the higher quantity of CSH crystals, all compared with the plain cement mortar, are all contributing towards a higher value of the tensile strength. Moreover, nanoclay particles attract cement particles and bond them together, thus obtaining a more durable composite [46,54].

It was also observed that the final tensile strength was also influenced by the curing method. Results on samples cured in water and samples cured by plastic wrapping were obtained and compared. Lower values of the tensile strength were obtained, especially after 90 days of curing, by applying the second method as the cement particles did not have enough water to fully hydrate. For 1% cement replacement with montmorillonite nanoclay, the difference between the two methods, in terms of strength, was 0.40 MPa at 90 days of curing [55].

The influence of temperature upon the cement mortar combined with 1 and 2 wt% natural hydrophilic montmorillonite sample was also investigated. It was observed that when the temperature increased up to 200 °C, the value of the tensile strength increased substantially for all samples, including the control sample. In case of 2% nanoclay cement replacement, a maximum difference of approximately 27% was reported between the values obtained for the tensile strength of the control sample and the nanoclay-cement composite, the nanoclay particles proving their efficiency. This increase in the value of the tensile strength was given by the chemical reactions which occurred during sample heating, namely the hydration acceleration, which promoted CSH formation around the nanoclay particles. As the temperature increased to 400 °C, the tensile strength dropped to 1.5–1.9 MPa for all samples. At 600 °C, a maximum value of approximately 0.2 MPa was obtained for the splitting tensile strength of the control mix. However, the nanoclay composite samples maintained consistently better values of the splitting tensile strength than the control one [18].

Table 1 summarizes the values of the tensile strength of mortar or concrete samples combined with different percentages of nanoclay, at room temperature, cured for 28 days in tap water or lime-saturated water.

Table 1. Splitting tensile strength values for different nanoclay-cement matrix samples.

Study	Type of Nanoclay	Type of Sample	Standard	w/b w/c	Additives	NC [%]	Tensile Strength [1] [MPa]
[18,56]	Natural hydrophilic montmorillonite	Cement mortar	ASTM C190	w/b 0.55	-	0	3.20
						0.5	3.30
						1	3.40
						2	3.50
[46]	Metakaolin	Cement mortar	ASTM C307	w/b 0.50	-	0	3.60
						2	4.05
						4	4.48
						6	4.92
						8	5.36
[54]	Metakaolin	Concrete	ASTM C496	w/c 0.42	1.5% polypropylene	0	7.96
						2	8.32
						4	9.54
						6	10.42
						8	11.16
						10	9.63
[55]	Montmorillonite (type not specified)	Concrete	ASTM C496	w/c 0.45	-	0	aprox. 4.30
						1	aprox. 5.80
						2	aprox. 5.50
						3	aprox. 5.10

[1] Some values were approximated from the graphics, associated with the cited scientific research.

All samples registered a growth in the values of the tensile strength as the percentage of nanoclay increased, except for the sample analyzed in [54]. In that case, at 10 wt% NC addition, the value of the strength decreased by 13.70%, compared to those obtained for an 8 wt% NC addition. Taking into account that the nanoclay percentage was very high, obtaining a homogeneous nanoclay dispersion becomes very difficult, leading to flocculation. This automatically creates weak points within the matrix. The values of the splitting tensile strength reported in [54] were higher than those presented in [55] due to the use of polypropylene fibers, which succeed in controlling the occurrence and the propagation of cracks. In the former case, the authors used nanoclay in order to obtain a better bond between the polypropylene fibers and the matrix [54]. Although nanoclay is not able to completely prevent the occurrence and propagation of fractures, the increase in the value of the flexural tensile strength of the composite leads to smaller and fewer cracks inside the material. Therefore, the reinforcement is protected from the ingression of chemical agents and humidity increasing the durability of reinforced concrete elements.

The results obtained for mortar samples follow the same trend as the ones reported for concrete [18,46,56]. The difference of 0.55 MPa for 2 wt% NC can be explained by the smaller water to binder ratio used for the former.

2.5.2. Flexural Tensile Strength

Taking into account that the bending state of loading is present in every civil engineering structure, the researchers had to verify if and to what extent the content of nanoclay would influence the flexural tensile strength of cement mortar or concrete elements. There are several studies on the improvement of the flexural strength regarding the combination between nanoclay and cement-based materials. The focus was on preventing or limiting the occurrence of cracks, which, besides the fact that this leads to the exposure of reinforcement to the outside air, the reinforcement could not benefit from the protection of the concrete cover in case of a fire.

In case of exposure to high temperatures, the same trend observed for the splitting tensile strength was reported in [18] for the flexural tensile strength, for 1 and 2 wt% natural hydrophilic montmorillonite cement replacement, without any treatments. For all

specimens and all temperatures, the 2 wt% NC composites exhibited the highest strength values compared with the control sample. The maximum flexural strength was reached at a temperature of 200 °C, at 11.60 MPa. When subjected to 400 °C, the flexural strength had a major drop in the value, of about 76% for the control sample, considering as reference the value for 200 °C, reaching a value of 2.60 MPa. The influence of nanoclay was evident at 400 °C, as the flexural strength value increased for 2 wt% NC by 138% compared to the control specimen. Unlike the tensile strength, the specimens preserved a certain value of flexural strength after their treatment at 600 °C, although very small—0.8 MPa for the control specimen. Adding 1 wt% NC, in this case, did not lead to flexural strength improvements, but for the 2 wt% NC combination the strength value reached 1.7 MPa [18].

A similar analysis was conducted for 1, 3 and 5 wt% nano-calcined montmorillonite clay [28]. The same trend of flexural strength increase was obtained at 250 °C, reaching the maximum value for 5 wt% nanoclay. At the next temperature stage, i.e., 450 °C, the strength decreased significantly for all specimens. It should be noted that at about 180 °C, polypropylene fibers started to melt and caused an increase in porosity which, in turn, led to smaller flexural strength values than the ones reported in [18].

A comparison was conducted between two types of curing methods applied to specimens with various percentages of nanoclay added in the cement matrix, i.e., water curing and plastic cover curing. The authors of the study observed that, similar to the tensile strength, the flexural strength value was smaller when curing the specimens by plastic wrapping than by immersing them in water. The major difference was obtained at 90 days of curing for 1 wt% NC sample, in which case the flexural strength decreased by approximately 14.9% for the second curing method compare to the traditional, water curing method [55]. This could be explained by the fact that the water cured specimens had enough moisture to continue the hydration process of the cement whereas the same process was significantly slowed down in case of plastic wrapping curing method once the mixing water was consumed.

Table 2 presents the values of the flexural tensile strength, for different inputs, regarding cement mortar and concrete composites with different nanoclay quantities. The values were selected for samples subjected only to room temperature and cured for 28 days in water or lime-saturated water.

Regarding what concerns the flexural strength for both cement mortar and concrete, the values vary significantly from one study to the other. The only common information resulted from these analyses would be the increase in the value of the flexural strength with the increasing nanoclay percentage within the cement matrix. The available data is sometimes conflicting, with some authors [28] reporting smaller values of the flexural tensile strength than others [18,56], although additives were used to improve workability and strength. One possible explanation could be the water to binder ratio. A w/b ratio of 0.55 could provide cement and nanoclay particles enough water to hydrate during mixing and curing period [18,56]. In another study [28], however, a lower w/b ratio was considered but a superplasticizer was used to improve workability. Generally, a small calculated w/b ratio provides a higher strength. However, due to the level of hydrophilicity of nanoclay, a higher amount of water could be needed. Moreover, there were two different types of montmorillonite used: a calcined one which was less hydrophilic and a natural one without treatment which had a high level of hydrophilicity.

Table 2. Flexural strength values for different nanoclay-cement matrix samples.

Study	Type of Nanoclay	Type of Sample	Standard	w/b w/c	Additives	NC %	Flexural Strength [1] [MPa]
[18,56]	Natural hydrophilic montmorillonite	Cement mortar	ASTM C348	w/b 0.55	-	0 0.5 1 2	7.40 7.60 7.60–7.70 7.80
[28]	Calcined hydrophilic montmorillonite clay	Cement mortar	ASTM C348	w/b 0.484	- non-absorbent monofilament polypropylene fibers - naphthalene-sulfonate-based superplasticizer	0 1 3 5	approx. 6.10 approx. 6.20 approx. 6.70 approx. 7.00
[54]	Metakaolin	Concrete	ASTM C293	w/c 0.42	1.95% polypropylene	0 2 4 6 8 10	9.36 9.92 11.24 12.02 12.76 11.50
[55]	Montmorillonite (type not specified)	Concrete	ASTM C78	w/c 0.45	-	0 1 2 3	approx. 5.00 approx. 6.60 approx. 6.30 approx. 5.90
[23]	Organo-montmorillonite clay	Cement mortar	ASTM C348	w/c 0.50	-	0 0.25 0.5 1	approx. 9.50 approx. 9.60 approx. 9.10 approx. 9.80

[1] Some values were approximated from the graphics, associated with the cited scientific research.

A decrease in the value of the flexural tensile strength for a higher percentage nanoclay was reported in [54,55], which may be due to the inhomogeneous specimens given by the large quantity of nanoclay present within the mixture. The values of the flexural tensile strength obtained by [54] on the concrete samples were higher for every nanoclay percentage, mainly because of the 1.5% polypropylene addition, which prevents crack formation and propagation.

The highest value of the flexural tensile strength from all the presented studies was reported by [23], although the authors did not use additives. This may be related to the organo-modified montmorillonite clay, which resulted after a treatment of the natural montmorillonite with dimethyl dehydrogenated tallow and quaternary ammonium chloride.

2.5.3. Compressive Strength

The most important material property of both cement mortar and concrete is their compressive strength.

Considering that there are several studies that investigated the variation in the compressive strength depending on temperature, the analysis within Section 2.5.3 pursues two directions. The first one will debate upon the compressive strength results obtained for specimens stored and tested at room temperature, while the second one will focus only on the studies where the specimens were subjected to elevated temperatures.

Strength Values at Room Temperature

From the data presented so far for splitting and flexural tensile strength, it was concluded that between the water curing and the plastic wrapping curing, the former is the best one to use for cement-based composites with nanoclay additions. The same trend was reported for the case of compressive strength. The latter curing method resulted in lower values of the compressive strength at 90 days, with on average a 14% decrease compared with water curing. As previously explained, cement and nanoclay particles need water to

hydrate and if they do not have enough, the hydration reaction significantly decreases and even stop and no C-S-H gels will be produced anymore, thus limiting the strength increase. The highest difference was observed at 90 days of curing. On the other hand, at the age of 28 days, this difference was very small [55].

In another study, the enhancement of compressive strength due to 1, 2, 3 wt% nanoclay addition in self-consolidating concrete was investigated [42]. The considered curing ages were 3, 7, 14, 28 and 90 days. The obtained results showed that the highest increment in the values of the compressive strength was at 7 and 14 days of curing, compared to the control mix. In that time interval the hydration process reached a maximum level, as the CH particles were consumed and CSH gels were formed. As more nanoclay was added in the cement matrix, the difference between the compressive strength of the control sample and the compressive strength of the nanoclay enriched composite became larger. A maximum was reached for 3 wt% nanoclay addition, the difference between the value of the compressive strength for the control mix and the nanoclay composite at 7 and 14 days of curing being 31% and 14%, respectively. For the 2 wt% nanoclay addition, this difference was 20.70% and 4.70%, respectively [42].

The compressive strength of a nanoclay-concrete composite at 7, 14, 28, 49, 56 and 90 days of curing, for nanoclay percentages of 0.1, 0.3 and 0.5 wt% and two water to cement ratios, i.e., 0.40 and 0.50, was also investigated. A similar trend was observed with the one reported in [42], the largest increase in the value of the compressive strength being during the first 28 days. The study also investigated the influence of water to cement ratio on the values of the compressive strength. The nanoclay percentage for which the maximum compressive strength was obtained changed depending on the w/c ratio. For a w/c ratio of 0.40, the optimum nanoclay percentage was 0.50%, whereas for a w/c ratio of 0.50, it decreased to 0.30% [57].

Table 3 summarizes the findings on the values of the compressive strength for mortar/cement specimens with certain percentages of nanoclay additions, stored at room temperature and cured for 28 days in water or lime-saturated water.

The smallest values for cement mortar reported in [28] can be explained by a non-homogeneous distribution of nanoclay within the cement matrix, the authors resorting to manual mixing of the material. This method can cause nanoclay particles to agglomerate and, eventually, lead to a decrease in strength. The same can be observed in terms of values of the flexural tensile strength obtained in [28] compared to other studies. In case of concrete, the results presented in [57] were very low in comparison with the other studies.

According to [57], for low nanoclay percentages, there was a negative influence upon the compressive strength of the composite. An addition of only 0.1 wt% nanoclay led to a decrease of 14% in the value of the compressive strength, for a w/c ratio of 0.50. However, when increasing the nanoclay content, the compressive strength value exceeded the one of the control specimen but not significantly [57]. For percentages greater than 0.1 wt% nanoclay, the compressive strength value increased with the increase in nanoclay content within the cement matrix. However, a small decrease in the values of the compressive strength at the maximum analyzed nanoclay percentage, of about 5.15%, compared to the previous percentage, was reported in [54,55]. Taking into account the spread of the reported results, it is difficult to provide a reason applicable to all scenarios. On the other hand, as the percentage of nanoclay increases, the distance between nanoclay particles decreases and, as they tend to attract each other, flocculation of nanoparticles may occur, which leads to a decrease in the strength of the material.

Table 3. Compressive strength values for nanoclay—mortar/concrete specimens at room temperature.

Study	Type of Nanoclay	Type of Sample	Standard	w/b w/c	Additives	NC %	Compressive Strength [1] [MPa]
[23]	Organo-montmorillonite clay	Cement mortar	ASTM C109	w/c 0.50	-	0 0.25 0.5 1	approx. 45.50 approx. 49.00 approx. 55.00 approx. 52.50
[28]	Calcined hydrophilic montmorillonite clay	Cement mortar	ASTM C109	w/b 0.48	- non-absorbent monofilament polypropylene fibers - naphthalene-sulfonate-based superplasticizer	0 1 3 5	approx. 21.00 approx. 21.20 approx. 22.00 approx. 24.10
[18,56]	Natural hydrophilic montmorillonite clay	Cement mortar	ASTM C109	w/b 0.55	-	0 0.5 1 2	37.00–37.60 38.00 38.50–39.00 40.30–41.00
[46]	Metakaolin MKC	Cement mortar	ASTM C109	w/b 0.50	-	0 2 4 6 8	approx. 47.20 approx. 47.60 approx. 48.50 approx. 49.70 approx. 50.50
[54]	Metakaolin MKC	Concrete	BS 1881 -Part 116	w/c 0.42	1.5% polypropylene	0 2 4 6 8 10	52.32 53.80 55.90 57.50 58.80 55.60
[55]	Montmorillonite (type not specified)	Concrete	ASTM C470	w/c 0.45	-	0 1 2 3	approx. 45.00 approx. 61.00 approx. 58.00 approx. 55.00
[42]	Montmorillonite (type not specified)	Self-consolidated concrete	-	w/b 0.34	F-type poly-carboxylate-based superplasticizer	0 1 2 3	approx. 49.20 approx. 52.00 approx. 51.00 approx. 54.50
[57]	type not specified	Concrete	-	w/c 0.40 ——— w/c 0.50	-	0 0.1 0.3 0.5 0 0.1 0.3 0.5	approx. 35.00 approx. 34.00 approx. 37.00 approx. 39.40 approx. 34.00 approx. 29.00 approx. 36.00 approx. 35.00

[1] Some values were approximated from the graphics, associated with the cited scientific research.

Strength Values at Elevated Temperatures

When concrete or cement mortar specimens are subjected to high temperatures, a temperature gradient develops inside the elements. The chemical and physical phenomena which occur lead to spalling or fracture development. Therefore, a decrease in strength is registered, the material losing its ability to overtake the induced thermal generated stresses.

Table 4 presents the compressive strength variation for different cement mortar/concrete specimens with nanoclay addition, cured for 28 days in water or lime-saturated water, subjected to various temperatures. Taking into account that the studies which are presented in this section were also reported in Table 3, the given information will focus only on the temperature variation and the corresponding values of the compressive strength.

Table 4. Compressive strength values for nanoclay—mortar/concrete specimens at high temperature.

		[18]			[28]			
Type of Nanoclay		**Natural Hydrophilic Montmorillonite**			**Calcinated Hydrophilic Montmorillonite**			
Nanoclay Content [%]		**0**	**1**	**2**	**0**	**1**	**3**	**5**
Compressive strength [1] [MPa]	25 °C	37.6	38.5	40.3	21	21.2	22	24.1
	200 °C	54.4	56.1	59.7				
	250 °C				22.5	23	24	27
	400 °C	38.9	40.2	41.6				
	450 °C				11	12	14	17
	600 °C	9.2	9.8	10.6	10	10.5	12	13.5
	900 °C				2	2.5	5	5

[1] All values are approximated from the graphics, associated with the cited scientific research.

As temperature reaches 200 °C, the value of the compressive strength increases, according to the data reported in [18] and graphically presented in Figure 3a due to the acceleration of the hydration process and the CSH production. The highest value was obtained for 2% nanoclay cement replacement—59.7 MPa. On the other hand, the rate of increase in the values of the compressive strength for the three considered mixes was between 44.68% for the control mix and 48.14% for the mix containing 2 wt% nanoclay cement replacement. As the temperature increased up to 400 °C, the material lost its strength by about 30% but it still maintained a value higher than the control specimen kept at room temperature. It is interesting to observe that in this case, the highest gain in the value of the compressive strength was obtained by the mix with 1 wt% nanoclay cement replacement, at 4.42%. At 600 °C, all samples registered a very high strength loss of about 75% with respect to the 400 °C samples, the 2% nanoclay combination having the biggest residual compressive strength value, i.e., 10.6 MPa [18].

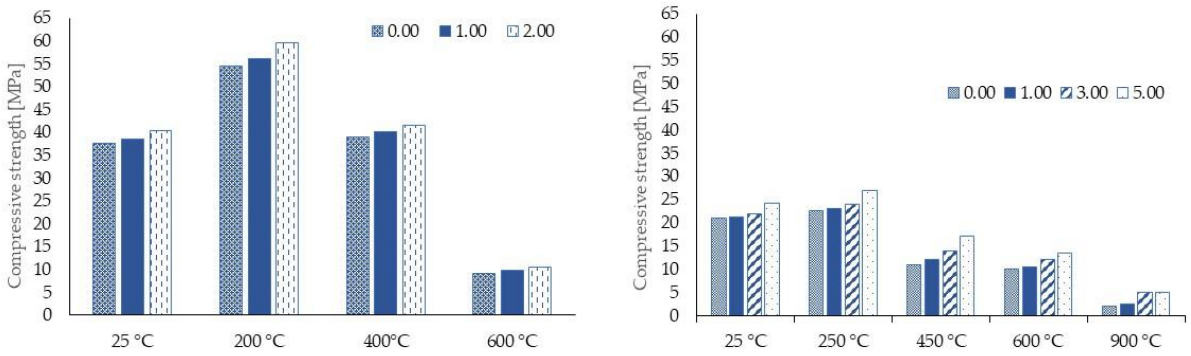


Figure 3. Variation in compressive strength as function of temperature and different percentages of nanoclay. (**a**) results reported in [18]; (**b**) results reported in [28].

Although the values were smaller than those presented in [18], the trend reported in [28] was similar for the cement mortar subjected to high temperatures, as seen in Figure 3b. The authors observed that as the temperature rose to 250 °C, the value of the compressive strength increased as well, as the hydration process is accelerated and more CSH is produced. For that temperature, the optimum nanoclay percentage was 5%. However, at 450 °C, the strength was already diminished significantly by about 37% compared to the 5% nanoclay cement replacement at 250 °C, when CSH was in the decomposing process. For 600 °C, there was an evident strength loss especially for the nanoclay-cement composite reaching a maximum of 20.6%. At 900 °C, the strength loss continued for all specimens but the nanoclay-cement composite still maintained a higher

strength value than the control sample. It should be noted that there was no difference in residual compressive strength between the 3% and 5% nanoclay cement replacement [28].

2.6. Durability Tests

The durability of a material is essential in civil engineering where the structures must have a life cycle of decades and where some of them are subjected not only to external loads but also to water penetration which can lead to corrosion, to frost-thaw cycles, to air with various chemical pollutants, etc. There are several studies that investigated the influence of nanoclay on the long-term durability of cement mortar or concrete.

Gas permeability tests with methanol were used [14] on samples made of cement paste with different quantities of montmorillonite nanoclay. As the curing period increased, the permeability coefficient decreased. There was a pattern emerging from this analysis that is common to all curing periods. The smallest permeability coefficient was registered for 0.4% nanoclay cement replacement, whereas the highest corresponds to the control specimen. The relative decrease was significant, a value of 49.95% being obtained for the 56 days curing period [14]. This result demonstrates the filler effect that nanoclay has on the cement matrix, succeeding in decreasing porosity and blocking outside elements to penetrate inside the cement matrix.

However, the results of the tests on cement pastes could not be confirmed by the results obtained on concrete specimens [41]. Nano-metakaolin was used in the concrete mixes and oxygen permeability tests were conducted. A higher permeability was obtained for nanoclay samples compared to the control samples, with approximately 150% for the 1% nanoclay and 200% for the 2% nanoclay. The difference between the two studies may have several explanations: different types of permeability tests, increased porosity due to the presence of aggregates combined with an insufficiently dispersion of nanoclay particles within the cement matrix, type of nanoclay, etc.

Water penetration and water absorption test are relevant when assessing the probability of water reaching the reinforcement and eventually causing corrosion. Tests were conducted in accordance to the EN 12390-8 norm and it was observed that for 1–3 wt% nanoclay cement replacement, the quantity of water penetrating the concrete samples was less than in case of the control samples, for which a 31 mm depth was registered [55]. The smallest depth of water absorption, i.e., 20 mm, was obtained for the 1 wt% nanoclay. The reasons for the smaller water depth values for concrete combined with nanoclay are the filler effect that nanoclay has coupled with the higher development of CSH gels compared to the control sample resulting in a denser structure of the material. The above results were obtained at the age of 28 days of water curing. In case of plastic wrapping curing, all samples had a higher water absorption than the control sample, which confirms the results obtained for compressive, flexural and tensile strengths [55]. Similar results were obtained for self-consolidated concrete with 1, 2 and 3 wt% nanoclay addition, with 90 days of curing [42]. However, the smallest water penetration depth was registered for 3% nanoclay addition, which was 64.3% smaller than the control specimen [42].

A water absorption test based on ASTM C642 for concrete specimens with 1, 2 and 3% montmorillonite nanoclay was also used [55]. As in the case of water penetration test, all nanoclay specimens had a water absorption percentage smaller than the control specimen. The lowest water absorption percentage corresponded to the 1% nanoclay sample, i.e., 1.46%, 54.3% smaller compared to the control sample [55]. Similar results were reported for self-consolidated concrete samples with 1, 2 and 3% nanoclay addition [42]. In contrast with [55], the lowest water absorption percentage corresponded to the 3% nanoclay mix while the highest was for 2% nanoclay. A possible explanation could be attributed to the effect of shrinkage on the integrity of the mix [42]. For cement mortar on the other hand, the obtained results were different, as the water absorption percentage for a 0.5% nanoclay addition was smaller than the one for the control specimen, but for 1% and 2% nanoclay, the value was higher and has an increasing trend [56]. The authors associated their results with the capillary water absorption test, in which case the specimens were

submerged in water only at 5–10 mm depth, according to BS EN 1015-18 norm. The lowest capillarity absorption coefficient results came from 1% and 2% nanoclay, reaching a value of approximately 0.03 kg/(m^2 min$^{0.5}$), compared with 0.04 kg/(m^2 min$^{0.5}$)—corresponding to the control sample [56].

When water trapped inside the cement matrix starts to evaporate, it creates pressure on the void walls which leads to the development of fine cracks. These cracks have a negative impact both on the strength and on the durability of the material. The influence of adding organo-montmorillonite nanoclay in the cement matrix upon the material plastic shrinkage was evaluated in [23]. It was concluded that nanoclay has a definite positive effect, as the plastic shrinkage value decreased by 70%, even for the lowest analyzed nanoclay quantity, i.e., 0.25 wt% cement replacement [23].

An impressed voltage test was employed to analyze the variation in corrosion current for self-consolidating concrete modified with 1, 2 and 3% nanoclay [42]. It resulted that, as the percentage of nanoclay increases, the deterioration time of the reinforcement extended, meaning that the use of nanoclay leads to a better protection of the steel reinforcement against corrosion mainly due to the denser structure of the cement matrix.

Table 5 summarizes the findings reported in this section of the paper. The information is structured based on the type of durability test, type of material it was conducted on (i.e., mortar or concrete) and nanoclay percentage. The main findings of each referenced study are also included.

Table 5. Durability tests on nanoclay—mortar/concrete specimens.

Measured Parameter	Scientific Paper	Test	Type of Sample	Type of Nanoclay	Nanoclay Percentage	Observation
Permeability coefficient	[14]	Gas permeability test (methanol)	Cement paste	Montmorillonite in liquid form (type not specified)	0; 0.2; 0.4; 0.6; 0.8	- As the curing period increased, the permeability coefficient decreased - The smallest permeability coefficient was registered for 0.4% nanoclay, and the highest for the control sample
	[41]	Oxygen permeability test	Concrete	Nano-metakaolin	0; 1; 2	- Higher permeability for nanoclay samples compared to control samples
Water absorption percentage	[55]	Water absorption test	Concrete	Montmorillonite (type not specified)	0; 1; 2; 3	- The test was carried out at 28 days of curing - Water absorption percentage smaller than the control specimen - The lowest value corresponds to 1 wt% nanoclay - Plastic wrapping curing samples had a higher water absorption than the water curing samples
	[42]	Water absorption test	Self-consolidated concrete	Montmorillonite (type not specified)	0; 1; 2; 3	- The test was carried out at 90 days of curing - Water absorption was reduced when nanoclay was added - The best result was for the 3 wt% nanoclay addition
	[56]	Water absorption test	Cement mortar	Natural hydrophilic montmorillonite clay	0; 0.5; 1; 2	- Water absorption percentage for 0.5% nanoclay was smaller compared to the control specimen - For 1 and 2% nanoclay, the value was higher than the control specimen

Table 5. *Cont.*

Measured Parameter	Scientific Paper	Test	Type of Sample	Type of Nanoclay	Nanoclay Percentage	Observation
Water penetration depth	[55]	Water penetration test	Concrete	Montmorillonite (type not specified)	0; 1; 2; 3	- The test was carried out at 28 days of curing - 1 wt% nanoclay—smallest depth of water absorption (20 mm) - Plastic wrapping curing samples had a higher water absorption than the water curing samples
	[42]	Water penetration test	Self-consolidated concrete	Montmorillonite (type not specified)	0; 1; 2; 3	- The test was carried out at 90 days of curing - The best result was for the 3 wt% nanoclay addition
Capillary water absorption coefficient	[56]	Water absorption test	Cement mortar	Natural hydrophilic montmorillonite clay	0; 0.5; 1; 2	- The lowest capillarity absorption coefficients resulted for 1 and 2% nanoclay
Plastic shrinkage	[23]	Plastic shrinkage test	Cement mortar	Organo-montmorillonite clay	0; 0.25; 0.5; 1	- Nanoclay has a definite positive effect - Plastic shrinkage decreased by 70% for 0.25 wt% nanoclay cement replacement
Corrosion current	[42]	Impressed voltage test	Self-consolidated concrete	Montmorillonite (type not specified)	0; 1; 2; 3	- As the percentage of nanoclay increases, the deterioration time of the reinforcement ex-tended

2.7. Remarks on the Impact of Using Nanoclay in Cement Composites

Nanoclay particles can be used in a modified or unmodified physical state, depending on their properties. From the scientific literature analysis, it can be stated that nanoclay has a positive impact as it succeeds in diminishing some of the weak points characteristic to mortar and concrete, the newly composite being characterized by:

- higher values of tensile, flexural and compressive strength, for both specimens kept at room temperature and subjected to high temperatures
- lower water absorption percentage and water penetration depth
- lower plastic shrinkage
- extended reinforcement deterioration time

The combined physical and chemical properties of nanoclay make this nanomaterial suitable for use in mortar/concrete mixes. Although all results concur to this idea, the values differ from one study to another, especially the ones related to the mechanical properties. At this moment, most of the related studies are focused on the cement paste. Therefore, there is a great gap of knowledge regarding mortar and, especially, concrete modified with nanoclay. Moreover, taking into account the promising values of compressive strength for specimens subjected to high temperatures and the lack of research in this area, more studies should be conducted on this subject.

3. Influence of Titanium Dioxide on Cement-Based Materials

The use of titanium dioxide (TiO_2) in the construction industry did not have a structural purpose in the beginning, but a more architectural and ecological one. Torre de Especialidades from Mexico City and the Jubilee Church in Rome Italy are two of the buildings for which titanium dioxide was used in the concrete formula with the purpose of decreasing the level of pollutants, i.e., nitrogen oxide and nitrogen dioxide. Except the practical application, the esthetics of these buildings stands out not only due to the architecture but also due to their bright whiteness [58–61].

As a nanomaterial, TiO_2 captured the interest of researchers in the fields of building services and electrotechnics. It started to be used in photovoltaic cells, in the composition of semiconductors and even in bio-medical applications and cancer therapy [62]. Moreover, as its properties have the potential to improve the strength and durability of cement mortar and concrete elements, the research in civil engineering is still on-going. The positive influence on both ecology and civil engineering is a material property which is constantly searched for, in view of the new stricter regulations in terms of greenhouse gas emissions. Titanium dioxide combines, at a certain level, these two areas of interest. In addition, TiO_2 is a naturally occurring oxide, being found in the Earth's crust [63], its addition to concrete enhancing the sustainability index of the new material [64].

3.1. Chemical Structure and Properties—Types of TiO_2 Used in Cement Mortar and Concrete

The crystalline structure of titanium dioxide, TiO_2, is found in three main different forms: anatase, rutile and brookite. Both anatase and rutile have a tetragonal crystal structure, while brookite has an orthorhombic crystal structure [63,65,66]. From these three crystal structures, the most commonly used in civil engineering are anatase and rutile. Both are wide band gap semiconductors, meaning that they can resist higher temperatures, unlike brookite [65,67].

Rutile is considered as the most stable form of titanium dioxide but only for a particle size greater than 35 nm. Below that size, the thermodynamic stability decreases. Another characteristic of rutile is its behavior at high temperatures. When the calcination temperature increases, its particle size increases also with a growth rate higher than in case of anatase [63]. Anatase, on the other hand, develops a higher photocatalytic activity than rutile and, thus, was preferred for various element coatings. Moreover, it was demonstrated that it has better success in breaking both inorganic and organic pollutants. On the other hand, it was shown that combining the anatase and rutile phases, leads to an increase in the photocatalytic activity [65,68]. This breaking of pollutants during the photocatalytic process begins when a light with enough energy strikes the material containing TiO_2, i.e., the catalyst, and an oxidation-reduction reaction takes place. During the process, the pollutants are mineralized, but the quantity of TiO_2 is not consumed. However, between 550 °C and 1000 °C anatase transforms into rutile, the transformation temperature depending on the existent impurities and the morphology of the sample [65,66,68].

Several general chemical properties of TiO_2 are listed in [66], with some of them making it adequate for use in mortar and concrete, such as its chemical stability, biocompatibility, low toxicity, and low cost compared with other nanomaterials.

3.2. Input of TiO_2 Particles in Cementitious Materials—Technological Flow

There are two possibilities of using TiO_2 combined with mortar or concrete. The first one is by introducing a certain quantity of nanomaterial in the cement matrix and mixing it. The other one is by coating the element with a special formula in order to protect the element from the exterior polluted environment. This study will focus on the first method, taking into account that the main interest is the material strength. Moreover, there is an important probability that the coating could be damaged during execution or service life [65]. Unlike nanoclay, titanium dioxide does not require any additional special mixing processes before being added to the cement matrix, as it does not have the tendency to flocculate. There are two methods of adding TiO_2 in the cement matrix, namely the wet and the dry mixing procedures.

In the first method, TiO_2 is introduced in water and mixed for several minutes. The cement and aggregates are mixed in dry conditions, separately. Afterwards, the water-nanomaterials solution is added to the dry mix, the rest of the water is added and a final mixing is performed. If there was fiber reinforcement to be added, e.g., PP fibers, it is introduced into the matrix in the final step and mixed again [58,69–71].

In the second method, the aggregates and all the powder materials, including TiO_2, are dry mixed together. The water is gradually introduced, along with the superplasticizer and mixed for 3–5 min until a proper consistency is reached [72–75].

3.3. Structural Influence of TiO_2

Similar to other nanoparticles, titanium dioxide nanoparticles have been used for their high specific surface area which can result in promoting the hydration reaction and for their pore-filling effect. In addition to these benefits, common to this size, TiO_2 has specific properties that make it attractive in its use in cementitious composites, such as its photocatalytic properties and thermal stability.

Titanium dioxide does not possess pozzolanic activity, as shown in several studies [59,76]. Nevertheless, it increases the rate of hydration due to the nanoparticles acting as nucleation sites. This process, together with the small size induced filling effect, creates a denser structure. It has been found that CH is influenced by the presence of these nanoparticles, which decrease the size of CH crystals either by limiting their growth space or by promoting accelerated CSH gels formation [59,76].

Studies on cement paste incorporating TiO_2 nanoparticles used TG analysis in order to render evident the hydration reaction acceleration [77]. It can be inferred that the pure cement specimen contains less non-evaporable water, chemically bound water, than the cement-titanium blend, which is a result of the presence of more hydration products [77].

3.4. Material Strength Improvements

Titanium dioxide nanoparticles succeed in improving the mechanical properties of cement mortar and concrete due to their chemical and physical properties. They are usually used in mortar/concrete mixes combined with superplasticizers in order to obtain a higher workability. Taking into account that TiO_2 is a non-reactive powder, there are studies in which pozzolans were added with the purpose of promoting the cement hydration reaction, e.g., fly ash, silica fume. In addition, in comparison with nanoclay studies, in the case of TiO_2, the number of scientific experiments made on mortars and concrete is significantly larger. This section of the state-of-the-art article presents the strength values of mortar and concrete modified with certain quantities of TiO_2 and other additives. The results will focus on the effect that TiO_2 has on the mortar and cement, with or without supplementary materials.

3.4.1. Splitting Tensile Strength

As in the case of nanoclay, the number of research works focusing on the tensile strength is less than in case of compressive strength. However, this mechanical property is also important, mainly from the point of view of cracks occurrence which must be prevented. Even micro-cracks can lead to an exponential decrease in the concrete and/or reinforced concrete durability. Due to the large specific surface area of TiO_2 particle there is more area available for the cement hydration reaction to occur and to produce more CSH, which leads to an increase in strength [78].

The value of the tensile strength of concrete when the cement was replaced with 1 wt% nano-TiO_2 was compared with the one obtained when the cement was replaced with 1 wt% nano-Fe_3O_4 [79]. The results showed that the TiO_2-modified specimen developed 18% higher values for the tensile strength. It should be noted that adding Fe_3O_4 to the mix results in values of the tensile strength smaller than the ones corresponding to the control specimen.

Other studies focused on the synergistic effect of using two nano-materials, e.g., both TiO_2 nanoparticles and carbon nanofibers (CNF) [80]. By adding only 0.2% and 0.4% of CNF in the cement matrix, the tensile strength values increased at about 3.90 MPa and 4.20 MPa, respectively. Compared with specimens containing only TiO_2, these values were much higher, proving that CNF have a higher efficiency in strength improvement than TiO_2. When introducing both CNF and TiO_2 nanoparticles in the composition, although

the values of the tensile strength were higher compared to the composite with a single type of nanomaterial addition, the dispersion deficiencies and particle agglomeration started to emerge. Thus, for the highest nanoparticle quantity combination considered, i.e., 0.4% CNF and 5% TiO_2, the tensile strength value was smaller than for the 0.4% CNF and 3% TiO_2 at 28 days of curing. Moreover, at 180 days of curing, the tensile strength value for the maximum nanoparticle combination became smaller than the composite having only 0.4% CNF and no TiO_2. Another remark that could be made regarding the values of the tensile strength for the 3% and 5% TiO_2 combination, after 90 days of curing, was that the difference between these values started to decrease slowly and reached almost the same value of 4.8 MPa at 180 days of curing [80].

In another study, ZnO and TiO_2 nanoparticles were used as supplementary materials to improve the mechanical properties of concrete containing 0.6% polypropylene fibers. The focus of the research work was to find the best combination for which a maximum strength was achieved. The cement was replaced with ZnO and TiO_2 in the following percentages: (1%; 0.5%), (2%; 1%), (3%; 1.5%), (4%; 2%), (5%; 2.5%). For the splitting tensile strength, the best combination was (4%; 2%), which proved that both ZnO and TiO_2 have a positive effect on the material properties. However, when the nanomaterials quantities were increased to (5%; 2.5%), a decrease in the values of the tensile strength was registered due to the problems in nanoparticles dispersion [71].

Table 6 lists a series of research works in which various cement mortar or concrete specimens modified with TiO_2 nanoparticles were tested to obtain the values of the tensile strength at 28 days of curing. It should be noted that the list focuses on the research works that used TiO_2 as principal nanomaterial.

Table 6. Splitting tensile strength values mortar/concrete specimens modified with TiO_2 nanoparticles, at room temperature.

Study	Type of TiO_2	Type of Sample	Standard	w/b w/c	Additives	TiO_2 %	Splitting Tensile Strength [3] [MPa]
[78]	Type not specified (probably anatase)	concrete	-	w/c 0.45	Sulphonated naphthalene formaldehyde (superplasticizer)	0 0.5 1 1.5	3.45 3.54 3.76 3.65
[79]	Type not specified (probably anatase/rutile combination)	concrete	-	w/c 0.57	-	1	3.36
[80]	Type not specified (probably anatase)	concrete	ASTM C496	w/c 0.45	Polycarboxylate-based HRWR [1] agent (superplasticizer)	0 3 5	approx. 3.00 approx. 3.60 approx. 3.30
[70]	White powder (probably anatase)	concrete	-	w/c 0.38	15% Silica fume Sika ViscoCrete-3425 superplasticizer	0 0.5 1 1.5	3.37 4.39 4.93 4.76
[81]	Type not specified (probably anatase)	concrete	ASTM C496	w/b 0.40	-	0 0.5 1 1.5 2	1.80 2.60 3.00 2.70 1.90
[82]	Type not specified (probably anatase)	SCC [2]	ASTM C496	w/b 0.40	Polycarboxylate (superplasticizer)	0 1 2 3 4 5	1.60 1.60 2.00 2.50 2.90 2.60

[1] High-range water reducer. [2] Self-compacting concrete. [3] Some values were approximated from the graphics, associated with the cited scientific research.

The main common observation of these studies is that for high nanoparticle quantities, the value of the tensile strength decreased. Two main reasons are given for this phenomenon in the scientific literature. The first one is the dispersion difficulties that emerge when adding high percentages of nanoparticles as it increases the probability of agglomeration occurring. The second one is that if the quantity of TiO_2 was greater than the quantity needed for CH hydration, an excess of silica would be found inside the cement matrix, leading to a decrease in strength [70,81]. This percentage varies, but the majority of the listed research works showed that 1% cement replacement with TiO_2 is the quantity for which a maximum value of the tensile strength was obtained in case of concrete specimens [70,78,81].

The highest values of the tensile strength compared to the other studies was reported in [70]. It this case, the addition of 15% silica fume proved its efficiency [70]. The lowest values were obtained for the self-consolidated concrete specimens and plain concrete, respectively, both modified with various TiO_2 percentages [81,82].

Altogether, the TiO_2 nanoparticle addition in the cement matrix leads to a definite increase in the values of the splitting tensile strength, as the specific surface area increases and CSH particles formation accelerates. However, the increment is not well defined as it depends on a series of variables which are different, usually, from study to study, e.g., additives, water/cement or water/binder ratio, type of cement, type of mixing, particle size etc.

3.4.2. Flexural Tensile Strength

The flexural strength for various combinations of CNF and TiO_2 nanoparticles added in concrete was also investigated [80]. All combinations had a higher strength value than the control sample. However, the specimens containing CNF had superior strength, whereas the 5% TiO_2 mix had the smallest strength value from the modified formula samples. When combining 0.4% CNF with 3% and 5% TiO_2, the highest flexural strength values were obtained. In case of flexural tensile strength, unlike the splitting tensile test results, all CNF mixes, including combinations, led to superior strength values, especially after 180 days of curing. Therefore, the combination 0.2% CNF and 5% TiO_2 registered, at 180 days of curing, a value of the flexural strength smaller than that of the sample with only 3% TiO_2. These results confirm the observations made in the case of splitting tensile strength, that as the quantity of nanoparticle increases above a certain critical level, the strength begins to decrease because silica accumulates within the matrix and particle agglomerations occur [80]. For the flexural strength tests carried out on ZnO and TiO_2 specimens, the best combination was (4%; 2%) [71].

Table 7 summarizes the values for the flexural tensile strength for a series of studies on concrete specimens modified with a certain quantity of TiO_2 nanoparticles, stored at room temperature, after 28 days of curing.

For the TiO_2 modified cement mortar, the values of the flexural tensile strength were higher than in the case of concrete specimens. When adding coarse aggregates, although the compressive strength increased, voids occurred at the interfacial transition zone, which tended to develop under tensile stresses. Therefore, these voids led to smaller values for splitting and flexural tensile strength. However, the nanoscale particles have a filler effect on the matrix due to their reduced size. They can enter these voids and reconstruct the ITZ so that the weak areas are reduced in size and the development of microcracks is either slowed down or completely arrested. This phenomenon was observed by comparing the strength increment when adding TiO_2 nanoparticles in the matrix, in both cement mortar and concrete, respectively. Higher strength differences were registered for concrete specimens when they were modified with TiO_2 compared with the control samples, i.e., greater than 1 MPa [80–82]. However, in case of cement mortar, these improvements in the flexural tensile strength remained smaller than 1 MPa [83–85].

Table 7. Flexural strength values mortar/concrete specimens modified with TiO_2 nanoparticles, at room temperature.

Study	Type of TiO_2	Type of Sample	Standard	w/b w/c	Additives	TiO_2 %	Flexural Strength [3] [MPa]
[80]	Type not specified (probably anatase)	concrete	ASTM C78	w/c 0.45	Polycarboxylate-based HRWR [1] agent (superplasticizer)	0 3 5	approx. 4.00 approx. 5.20 approx. 4.50
[83]	Type not specified (probably anatase)	Cement mortar	ASTM C293	w/b 0.485	30% Fly ash by weight of cement	0 1 3 5	approx. 5.15 approx. 5.15 approx. 5.70 approx. 5.15
[81]	Type not specified (probably anatase)	concrete	ASTM C293	w/b 0.40	-	0 0.5 1 1.5 2	4.40 5.10 5.50 5.40 5.10
[82]	Type not specified (probably anatase)	SCC [2]	ASTM C293	w/b 0.40	Polycarboxylate (superplasticizer)	0 1 2 3 4 5	4.20 4.00 4.90 5.60 6.30 6.00
[84]	anatase	Cement mortar	Chinese standard	w/c 0.32	-	0 0.1 1	10.10 10.80 9.60
[85]	anatase	Cement mortar	ASTM C348	w/b 0.40	GGBFS [2] Polycarboxylate (superplasticizer)	0 3 6 9 12	approx. 5.30 approx. 5.50 approx. 4.40 approx. 4.00 approx. 3.80

[1] High-range water reducer. [2] Ground granulated blast furnace slag. [3] Some values were approximated from the graphics, associated with the cited scientific research.

Experiments conducted based on the Chinese standard resulted in the highest flexural strength values, reaching up to 10 MPa for cement mortar [84]. However, the researchers who used ASTM norms, whether or not additives were used, obtained values in the range of 4.0–6.0 MPa [80–83,85].

Taking into account the variability in TiO_2 percentages from one study to another and the difference in results, there is no optimum percentage which can be clearly defined. Smaller percentage increments, i.e., smaller than 1%, should be selected and the range of their variability should be larger in order to be able to thoroughly analyze the dependency between strength and the quantity of TiO_2 introduced. However, there is a certain trend which is also respected in the case of flexural tensile strength, namely, as the quantity of TiO_2 exceeded a certain level, the value of the flexural strength decreased.

3.4.3. Compressive Strength

The most important material property of both cement mortar and concrete is their compressive strength. As in the case of nanoclay, some studies subjected the specimens to high temperatures while others analyzed the samples only at room temperature. Taking into account that the high temperature tests are conducted in steps, for different temperature levels, corresponding to various physical and chemical phenomena, they are separately presented in the present paper.

Compressive Strength Values Obtained at Room Temperature

In case of compressive strength, a similar trend of the results was obtained as for flexural strength [80]. The CNF modified concrete exhibited the highest values of the compressive strengths compared with the specimens modified only with TiO_2. However, the maximum strength from the analyzed samples corresponds to a concrete specimen modified with both CNF and TiO_2 nanoparticles, i.e., 0.4% CNF and 3% TiO_2. Similar to the flexural tensile strength, the samples of CNF+ TiO_2 having 5% TiO_2 exhibited lower compressive strength value than the corresponding CNF modified concrete samples but without the TiO_2 addition. The trend was maintained at least up to 180 days of curing. Moreover, for the 0.2% CNF and 5% TiO_2, the registered values of the compressive strength was smaller than the 3% TiO_2 mix, at 28 days of curing [80].

Unlike the tensile strength case, the compressive strength of the 1% TiO_2 concrete specimens was lower than for the 1% Fe_3O_4 concrete specimens [79]. TiO_2 was used in combination with ZnO and 0.6% polypropylene fibers PPF to improve the concrete formula [71]. Samples were tested in compression according to the Indian standard IS: 516–1959. For both mixes, with or without PPF, the best nanomaterial combination was (4%; 2%) by weight of cement, the result being applicable for all curing ages (7, 14, 28 and 90 days). For the largest nanomaterial quantity, i.e., 5% ZnO and 2.5% TiO_2, the compressive strength value decreased at all ages below the values corresponding to the control sample [71].

Table 8 summarizes the values of compressive strength for concrete specimens modified with TiO_2 nanoparticles, kept at room temperature, and cured for 28 days.

The importance of TiO_2 nanoparticle dimension on the compressive strength value of cement mortar was demonstrated in [77]. The study employed two types on TiO_2, with dimensions of 21 nm and 350 nm. The mortar modified with larger TiO_2 particles had smaller values for the compressive strengths than the one with 21 nm. As the particle dimension increased, the specific surface area decreased, being promoted less CH for hydration and thus, less CSH in the cement matrix.

All samples registered a decrease in the values of mechanical properties after a certain TiO_2 quantity when the high number of particles increased the probability of flocculation and thus stress concentrations could occur. Moreover, as in the nanoclay case, when introducing a higher quantity of nanomaterial than the one needed for CH hydration, an excess of silica is available, resulting in a deficiency in strength [70]. The TiO_2 optimum percentage, from which this decrease initiated, and emphasized in Table 8, is not well defined when considering all the studies. It varies from 1% to 6% by weight of cement. High compressive strength was also obtained at 10%, according to [77], but there were no higher TiO_2 percentages analyzed, so there is no specific optimum TiO_2 percentage.

On the other hand, a previous study [60] reported that the values of the compressive strength decreased with the increase of TiO_2 percentage. Taking into account that the TiO_2 percentages analyzed in that study were relatively high, i.e., 5% and 10%, there is a high probability that the main cause of the obtained results was the agglomeration of nano particles during the mixing procedure.

To sum up, the compressive strength results presented in Table 8 demonstrate the positive effect that TiO_2 particles have on the cement mortar/concrete compressive strength. Unlike the case of the flexural tensile strength, there is no significant difference between the values of the compressive strength concrete and mortar, due to the fact that, during compression, the voids present in the ITZ tend to close.

Table 8. Compressive strength values mortar/concrete specimens modified with TiO_2 nanoparticles, at room temperature.

Study	Type of TiO_2	Type of Sample	Standard	w/b w/c	Additives	TiO_2 %	Compressive Strength [3] [MPa]
[80]	-	Concrete	ASTM C39	w/c 0.45	Polycarboxylate-based HRWR [1] agent (superplasticizer)	0	approx. 33.00
						3	approx. 42.00
						5	approx. 37.00
[83]	-	Cement mortar	ASTM C109M-16a	w/b 0.485	30% Fly ash by weight of cement	0	approx. 26.50
						1	approx. 33.00
						3	approx. 36.50
						5	approx. 30.70
[81]	-	Concrete	ASTM C39	w/b 0.40	-	0	36.80
						0.5	41.90
						1	43.40
						1.5	42.50
						2	39.30
[82]	-	SCC[2]	ASTM C39	w/b 0.40	Polycarboxylate (superplasticizer)	0	31.60
						1	35.20
						2	38.30
						3	44.50
						4	50.10
						5	48.70
[79]	-	Concrete	-	w/c 0.57	-	1	approx. 31.00
[85]	anatase	Cement mortar	ASTM C109	w/b 0.40	GGBFS [2] Polycarboxylate (superplasticizer)	0	approx. 40.00
						3	approx. 44.00
						6	approx. 46.00
						9	approx. 42.00
						12	approx. 36.00
[77]	75% anatase and 25% rutile (21 nm)	Cement mortar	ASTM C109	w/c 0.485	-	0	approx. 39.50
						5	approx. 47.50
						10	approx. 49.00
	99% anatase (350 nm)					5	approx. 43.00
						10	approx. 44.50
[69]	Rutile and anatase	Cement mortar	-	w/b 0.45	-	0	43.70
						1	47.60
						3	48.20
						5	48.80
[86]	Anatase and rutile—Aeroxide P25	High strength mortar	ASTM C109	w/b 0.35	2% naphthalene sulfonate base superplasticizer 5% silica fume	0	approx. 55.00
						1	approx. 63.00
						2	approx. 64.00
						3	approx. 61.00
[70]	White powder (probably anatase)	Concrete	-	w/c 0.38	15% Silica fume Sika ViscoCrete-3425 superplasticizer	0	49.86
						0.5	55.74
						1	58.79
						15	57.42
[60]	80% anatase and 20% rutile	ECC [1]	ASTM C109	w/c 0.30	PVA [2]	0	66.53
						5	60.05
						10	58.49
[78]	-	Concrete	-	w/c 0.45	Sulphonated naphthalene formaldehyde (superplasticizer)	0	33.00
						05	35.00
						1	38.00
						1.5	30.00
[75]	-	Concrete	BS 1881-part 116	w/c 0.40	Superplasticizer	0	34.00
						2	41.40
						4	44.20
						6	48.40
						8	46.50
[76]	-	Cement mortar	-	w/c 0.50	-	0	approx. 50.00
						1	approx. 50.00
						2	approx. 52.00
						5	approx. 48.00

[1] Engineered cementitious composite. [2] Polyvinyl alcohol fibers. [3] Some values were approximated from the graphics, associated with the cited scientific research.

Compressive Strength Values at Elevated Temperatures

Considering the filler effect that titanium dioxide has upon the cement matrix, along with promoting of the development of hydration compounds, it has been proven that the TiO_2 introduction in the cement matrix succeeded in improving the material strength to

elevated temperatures. Table 9 presents some of the compressive strength results on cement mortar/concrete when the specimen was subjected to elevated temperatures.

Table 9. Compressive strength values for TiO_2—mortar/concrete specimens at high temperature.

		[86]				[87]			
TiO_2 [%]		**0**	**1**	**2**	**3**	**0**	**2**	**4**	**6**
Compressive strength [1] [MPa]	25 °C	55	63	64	61	33	36.3	46.2	48
	100 °C	47	58	62	54				
	200 °C	46	52	58	51	38	43.5	47	54
	300 °C	35	46	51	48				
	400 °C	35	47	49	44	35	42	46	51.5
	600 °C	31	37	35	31	25	31	33.5	38.5
	800 °C	17	17	22	17				
	1000 °C	6	6	7	5				

[1] All values are approximated from the graphics, associated with the cited scientific research.

A high strength mortar was modified with 1%, 2% and 3% Aeroxide P25, i.e., a multiphasic titanium dioxide containing both anatase and rutile. A 5% silica fume and a superplasticizer were added in the mix. The water to binder ratio was maintained at 0.35 [86]. On the other hand, another study focused on heavy concrete samples, having a density greater than 2600 kg/m^3 with magnetite aggregates of 25 mm maximum size. The authors modified the samples by adding 2%, 4% and 6% TiO_2 as a cement replacement [87]. Although the difference between the values obtained in the two studies was expected to occur, the positive influence of TiO_2 is evident in both cases.

However, while a 2% TiO_2 was obtained as the optimum percentage for the compressive strength of, for all temperatures [86], as shown in Figure 4a, the maximum strength was recorded at the maximum nanoparticle addition of 6% [87], as seen in Figure 4b. Taking into account the use of magnetite aggregates, they will have a different behavior to high temperatures than the normal aggregates used in previous studies. Moreover, only fine aggregates were used in [86], thus obtaining a more homogeneous sample with less voids and less disturbances than in [87]. Therefore, a comparison between these two studies can be made only by analyzing the positive variation that TiO_2 had on the samples. Although the compressive strength decreased for the 3% TiO_2 sample, it still remained higher than the one corresponding to the control sample up to 400 °C [86]. After this temperature limit, the compressive strength maintained a value approximately equal with the one associated to the control specimen.

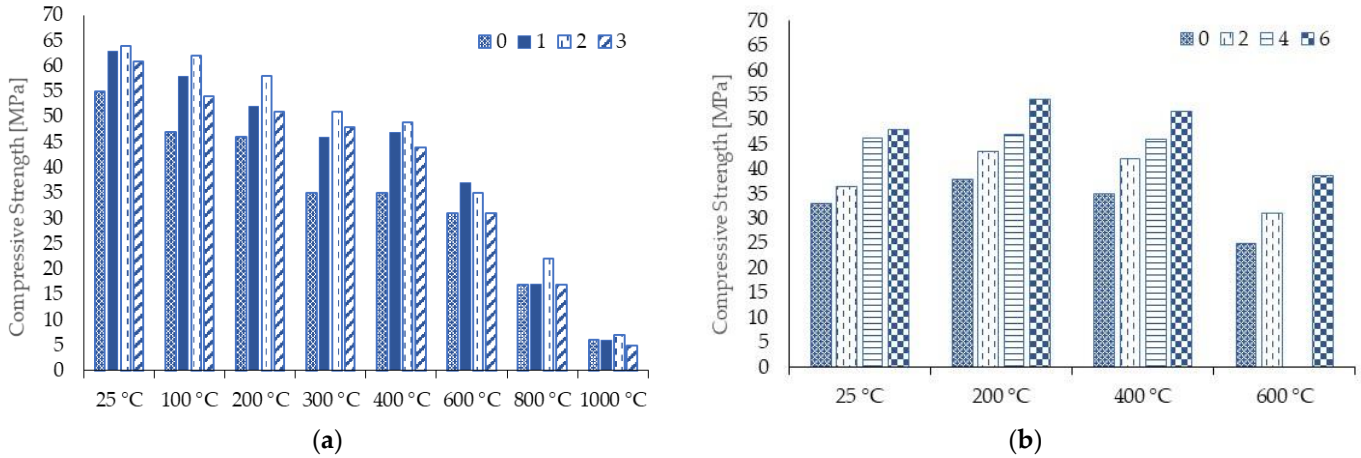


Figure 4. Variation in compressive strength as function of temperature and different percentages of TiO_2. (**a**) results reported in [86]; (**b**) results reported in [87].

3.5. Durability Tests

When the TiO_2 nanoparticles are introduced in the cement matrix, due to their small size, they start filling the existent voids, gathering around them CH compounds and promoting the CH hydration. Thus, the density of the specimen increases and water absorption is expected to decrease. For the anatase-based modified cement mortar used in [85], a constant decrease in water absorption up to the maximum considered TiO_2 percentage, from approximately 9%—for 0 wt% TiO_2, to 7%—for 12 wt% TiO_2 was recorded. These results were confirmed by [82]. A comparison between the influence of 1% Fe_3O_4 and 1% TiO_2 on concrete water absorption was conducted in [79]. From the analysis, nano-titania particles succeeded in restricting the water absorption better than Fe_3O_4, also having a smaller void ratio.

As the water absorption and void ratio decreased, the probability of liquid infiltration was significantly reduced, as the chloride and sulphate exposure analyses proved. A higher level of steel reinforcement corrosion protection was gained by using nano-TiO_2 as supplementary material in concrete, according to [79]. The potentio-dynamic polarization test confirmed the benefits of using TiO_2 in the cement matrix as the reinforcement corrosion rates were lower for all adverse exposure environments studied (tap water, saline water, acidic solution), compared to the control specimen [69].

However, it was recommended that all cementitious materials using nano-titania as additive should be specially designed to sulphate attack, as the expansion rate of the mortar increased with the quantity of TiO_2 and important cracks occur, compared to the control sample [85].

Table 10 summarizes the findings in terms of durability tests on mortar and concrete samples enhanced with TiO_2.

Table 10. Durability tests on TiO_2—mortar/concrete specimens.

Measured Parameter	Scientific Paper	Type of Sample	TiO_2 Percentage	Observation
Water absorption percentage	[85]	Cement mortar	0; 3; 6; 9; 12	- Decrease in water absorption with the increase in TiO_2 content
	[82]	SCC	0; 1; 2; 3; 4; 5	- During the first 2 days, the water absorption percentage increased compared to the control sample - For 7 and 28 days of curing, the water absorption percentage decreased compared to the control sample
	[79]	Concrete	1	- Nano-TiO_2 particles restrict water absorption better than Fe_3O_4
Durability to chloride and sulphate ions (corrosion potential)	[79]	Concrete	1	- Nano-TiO_2 leads to a higher level of steel reinforcement corrosion protection than Fe_3O_4
	[69]	Cement mortar	0; 1; 3; 5	- Reinforcement corrosion rates were lower for all adverse exposure environments studied compared to control samples - The optimum TiO_2 percentage was 5 wt%
Expansion rate	[85]	Cement mortar	0; 3; 6; 9; 12	- The expansion rate of the mortar increases with the quantity of TiO_2 and important cracks occur, compared to control sample

3.6. Remarks on the Impact of Using TiO_2 in Cement Composites

Titanium dioxide is a nanomaterial with multiple benefits, in various areas of interest, which has proven its significance in the field of civil engineering. Its nano-sized structure characterized by a large specific surface area promotes the acceleration of the CH hydration activity. Its filling effect, together with a high quantity of hydration products, i.e., CSH, results in higher values of compressive, flexural and splitting tensile strength compared to the control specimens. The filling effect also decreases the void ratio and the water absorption, increasing the reinforcement protection against tap/saline water or acidic solutions.

4. Conclusions

Nanomaterials have proven their benefits when used in cement mortar or concrete. Their size and chemical properties largely improve the strength and physical characteristics of cementitious composites. Nanoclay acts as a pozzolanic and filler nanomaterial, while titanium dioxide is an inert filler and promotor of nucleation sites for CSH development. Both nanoclay and titanium dioxide nano-particles succeed in promoting CH hydration when added to the cement matrix, thus leading to strength improvements. The water absorption decreases as well as the void ratio, increasing the reinforcement protection to corrosion. For both of them, the behavior is enhanced when subjected to high temperatures, compared with the control samples. Practically, they both improve the mechanical and physical characteristics of cement mortar and/or concrete. However, the manner in which this improvement is manifests varies.

The use of NC definitely influences the values of the splitting tensile strength for both mortar and concrete in a positive manner. However, the magnitude of this improvement greatly varies from one study to another because of the type of NC used and water/binder ratio. However, the use of montmorillonite-based NC shows its influence at lower percentages by weight of cement, for both mortar (2 wt%) and concrete (1 wt%), than metakaolin based NC (8 wt%). Based on the analyzed data, the rate of improvement also greatly depends on the water/binder ratio.

Similar conclusions can be drawn in terms of flexural tensile strength of cement-based mortar and concrete. For mortars, both natural hydrophilic montmorillonite and organo-montmorillonite based NC shown similar rates of improvement, compared to the reference mix, for 2 wt% replacement of cement for natural hydrophilic montmorillonite NC and 1 wt% replacement for organo-montmorillonite based NC. On the other hand, the use of calcinated hydrophilic montmorillonite NC leads to highest values in terms of flexural tensile strength of mortars when used in 5 wt% replacement of cement. For concrete mixes, metakaolin based NC should be used in higher percentages (8 wt% of cement) to obtain the highest values for the flexural tensile strength as compared to montmorillonite NC which leads to the best results at only 1 wt% of cement.

The compressive strength of both mortar and concrete are positively influenced by the addition of nanoclay, but the rate of improvement is different from mortar to concrete. Lower percentages of montmorillonite-based NC are required to obtain the highest values of compressive strength compared to metakaolin based NC. While for the former the highest values of the compressive strength of mortar are obtained at 0.5 wt% in case of organo-montmorillonite and up to 5 wt% in case of calcinated hydrophilic montmorillonite NC, in case of metakaolin based NC a higher percentage is required, 8 wt% of cement. Similar observations can be made for concrete, although the exact type of NC is not clearly specified. For montmorillonite-based NC the percentage varies between 1 wt% and 3 wt%, while for metakaolin based NC the percentage stays unchanged, namely at 8 wt% of cement.

The loss of compressive strength at elevated temperatures is inversely proportional to the percentage of NC in concrete. Based on the available scientific data, the peak performance is reached for 2% natural hydrophilic montmorillonite NC at 200 °C, while a similar trend is observed at 5% calcinated hydrophilic montmorillonite NC at 250 °C.

In case of durability of cement mortar and concrete, the best values are reached for much lower values of NC percentages than in the case of mechanical properties. Most of

the available scientific literature reporting results on durability performance of nanoclay modified mortar and concrete focuses on the use of montmorillonite-based NC. Significant improvements are obtained for percentages as low as 0.4 wt% of cement.

On the other hand, titanium dioxide, with a smaller particle dimension, is only an inert filler which does not have the possibility to promote pozzolanic activity as nanoclay does. The CH hydration, in this case, is accelerated only by the nucleation effect.

Most of the studies related to the use of TiO_2 in cement-based mortar and concrete used anatase based nano TiO_2. Therefore, the scattering of the reported results in terms of the optimum content of TiO_2 is smaller compared to their counterparts using NC.

From the point of view of the splitting tensile strength most of the studies recommend an optimum percentage of 1 wt% of cement in order to obtain the highest increase in performance for regular concrete. Self-compacted concrete, on the other hand, requires a higher percentage of nano TiO_2, up to 4%.

For the flexural tensile strength, the use of nano TiO_2 in 3 wt% of cement results in the highest values both for mortar and concrete. In this case however, there seems to be a large discrepancy of the obtained results depending on the standard applied.

When it comes to the compressive strength, although improvements were reported for both mortar and concrete with nano TiO_2 addition, the reported results in terms of optimum nano-TiO_2 content varies significantly from one study to another. While for concrete the optimum percentage varies from 1 wt% of cement up to 6 wt% of cement, with most of the studies recommending 1% addition of nano TiO_2 for best performance gains, the interval is much larger in case of mortar. In this case, the optimum percentage varies from 2 wt% of cement and up to 10 wt% of cement. It should be pointed out that the larger recommended interval is due to the fact that the input parameters significantly changed from one study to another: supplementary cementitious materials (fly ash, GGBS, silica fume), type of TiO_2 (anatase and combinations of anatase and rutile in different percentages).

The decrease in the compressive strength values of concrete with nano TiO_2 subjected to elevated temperatures followed a similar trend with the one reported for NC. The use of higher percentages of nano TiO_2 resulted in significantly lower strength losses with the increase in temperature compared to the reference mix. The temperature threshold beyond which strength loss become significant is similar to the one reported for NC, namely 400 °C. This suggests that, in case of elevated temperatures, the limitation is related to the behavior of cement rather than the other constituent materials.

In terms of durability performance of mortar and concrete, the optimum percentage varies from one study to another. According to the available data, a 5 wt% of cement leads to the best performance in durability tests. Higher percentages result in slightly better performance but the benefit is not as significant, percentage-wise.

Each of the two nanomaterials presented in this study lack some properties from the other, while having other similar effects on the cementitious materials. Therefore, a combination of these two types of nanoparticles has the potential of improving the mortar and/or concrete properties beyond the level set by each nanomaterial on its own due to their synergistic effect. While the synergistic effect of using TiO_2 in combination with silica fume [70], CNF [80], fly ash [83] and GGBS [85] was rendered evident in some previous studies, the use of TiO_2 in conjunction with nanoclay was not so intensively studied and only recently a very limited number of studies emerged in this direction.

A recent study proved the potential of this combination by adding to concrete 1%, 2%, 3% and 4% nanoclay as fine aggregate and 1%, 2%, 3% and 4% TiO_2 as cement replacement. The best results were obtained for the 2%-TiO_2 and 3%-nanoclay combination, with a compressive strength increment of 48.64% compared to the control sample and 21.83% increment compared to the concrete modified with only 2% TiO_2 [88].

A similar research work investigated the combined used of TiO_2 and NC in fly ash geopolymer concrete [89]. The main difference between this study and the previous one resides in the fact that lower percentages were used; only 1% NC and 1.25% TiO_2, by mass of fly ash. Improvements were observed in the values of splitting tensile and compressive

strengths of investigated mixes. The SEM images revealed the absence of interfacial voids and crack in the ITZ and the formation of needle-like structures at the interface regions between paste and aggregates. Those formations were attributed to pozzolanc interaction between the nanomaterials and the promotion of the nucleation sites.

Both aforementioned studies showed that better material properties can be obtained when TiO_2 and NC are used together, compared to the case when they are individually used and that lower percentages of the two nanomaterials are needed to obtain those improved material properties compared to each nanomaterial used individually. However, there is a lack of research on this combination of nanomaterials, which, taking into account their beneficial potential, should be studied further.

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