INFLUENCE OF TiO_2 NANOPARTICLES ON THE PHYSICO-MECHANICAL PROPERTIES OF CEMENTITIOUS COMPOSITES – EXPERIMENTAL RESULTS

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ABSTRACT

Urban constructions are subject to deterioration and degradation due to the action of external factors, pollutants from air, water, compounds resulting from the combustion of fuels used for heating and transport, etc. currently, worldwide, the possibility of building cementitious composite materials with self-cleaning properties is reported due to the photocatalytic capacity of TiO2 nanoparticles, used as an addition or as a substitute for a part of cement. The aim of this paper is to present experimental research on the influence of the introduction of titanium dioxide nanoparticles (TiO2) on some physico-mechanical properties of cementitious composites. Experimental research has been carried out on cementitious composite material containing TiO2 nanoparticles respectively the evolution of the following parameters was analysed: setting time, apparent density, absolute density, porosity, water absorption, water absorption by capillarity and white degree. The main objective of this study was to analyse the influence of the presence of titanium dioxide (TiO2) nanoparticles on the physico-mechanical properties of cementitious composites.

Keywords: TiO_2 nanoparticles; physico-mechanical properties; self-cleaning.

REZUMAT

Construcțiile urbane sunt supuse deteriorării și degradării ca urmare a acțiunii factorilor externi, a poluanților din aer, apă, a compușilor rezultați din arderea combustibililor utilizați pentru încălzire și transport etc. În prezent, la nivel mondial, posibilitatea de a construi materiale compozite cementoase cu proprietăți de auto-curățare este posibilă datorită capacității fotocatalitice a nanoparticulelor TiO2, utilizate ca o completare sau ca un substitut pentru o parte din ciment. Scopul acestei lucrări este de a prezenta cercetări experimentale asupra influenței introducerii nanoparticulelor de dioxid de titan (TiO2) asupra unor proprietăți fizico-mecanice ale compozițiilor cementoase. S-au efectuat cercetări experimentale asupra materialului compozit care conține nanoparticule TiO2, respectiv a fost analizată evoluția următorilor parametri: timpul de priză, densitatea aparentă, densitatea absolută, porozitatea, absorbția apei, absorbția apei prin capilaritate și gradul de alb. Obiectivul principal al acestui studiu a fost de a analiza influența prezenței nanoparticulelor de dioxid de titan (TiO2) asupra proprietăților fizico-mecanice ale compozițiilor cementoase.

Cuvinte cheie: nanoparticule TiO_2; proprietăți fizico-mecanice; auto-curățare.

1. INTRODUCTION

Urban constructions are subject to deterioration and degradation due to the action of external factors, pollutants from air, water, compounds resulting from the combustion of fuels used for heating and transport, etc. Currently, worldwide, the possibility of building cementitious composite materials with self-cleaning properties is reported due to the photocatalytic capacity of TiO_2 nanoparticles, used as an addition or as a substitute for a part of cement. It also raised awareness of the importance of building sustainability and thus felt the need for a material with self-cleaning properties mainly used in urban areas to ensure a cleaner environment and reduce maintenance costs. The use of this type of material leads to a reduction in the cost of maintenance, cleaning, repair, reduction of pollution due to their ability to decompose organic substances and the inorganic substances, the reduction of pollution as a result of the increase of the duration of the service, and to increase the time limits for the work of repair/maintenance, and increase the sustainability of the construction industry.

Research in the literature has shown that in general, it is recommended that TiO_2 nanoparticles are added dry, by mixing them directly with cement powder, then adding moisturizing water. It does not react chemically with any crystallographic form of titanium dioxide nor does a reaction occur between photosensitive nanoparticles with cement phases, therefore hydrolysis hydration reactions are not influenced (Folli, 2010; Hegyi et al., 2018; Grebenișan et al., 2019a, 2019b). A series of research has also shown that, adding TiO_2 nanoparticles influences the properties of fresh concrete. The first effect observed in the preparation of cement-based mortars and concrete is the increase in water needs to achieve the standard consistency (Janus et al., 2016; Zhao et al., 2015). Some research shows that by adding a maximum of 1% TiO_2 in the cementitious matrix does not significantly influence the fluidity (Kadri et al., 2002).

Regarding the influence of TiO_2 nanoparticles on workability, studies shown a decrease of this parameter with the increase of the percentage of TiO_2 nanoparticles in the mixture (Rashad, 2015). However, some research has indicated that by adding a maximum of 1% TiO_2 does not significantly influence the workability (Sorathiya et al., 2017). When introducing different ratios of TiO_2 nanoparticles in the mixture, it has been observed that the initial and final setting time decreases with the increase of TiO_2 nanoparticles (Rashad, 2015; Grebenișan et al., 2019a, 2019b).

The decrease in both workability and setting time as the quantity of TiO_2 nanoparticles introduced into the cement paste increases, can be explained by the catalyst effect that nanoparticles have on the cement hydration reaction and by the fact that they can function as potential core of accumulation of hydration products.

Literature indicates a reduction in porosity as the amount of nanoparticles in the cementitious mixture increases, with changes in the size and orientation of the crystals of cement hydration products and the formation of a greater amount of C-S-H gel (Janus et al., 2016; Sorathiya et al., 2017).

With the increase in the amount of nanoparticles a reduction of water absorption can also be observed, 0.5% being the optimal addition of nanoparticles if water absorption is evaluated at the age of 28 days and 90. If water absorption is assessed 7 days after casting, the optimal amount TiO_2 nanoparticles in the mixture are 4%. However, if water absorption is assessed 2 days after casting, the addition of TiO_2 nanoparticles increases the percentage of water absorption (Rashad, 2015).

Regarding the assessment of water absorption on the surface, the literature specifies that high (photochemically induced) wettability will result in a high potential for water absorption on the surface (Aslanidou et al., 2018; Graziani et al., 2014; Wang et al., 1999).

The aim of this paper is to present experimental research on the influence of the introduction of titanium dioxide nanoparticles (TiO_2) on some physico-mechanical properties of cementitious composites.

2. MATERIALS AND METHODS

Experimental research on cementitious composite materials containing TiO_2 nanoparticles carried out in the current research aims to study the evolution of the following parameters: setting time, apparent density, absolute density, porosity, water absorption, capillary water absorption, white degree and surface water absorption.

For this purpose, the working methodology consisted in the preparation of cementitious mixtures using white Portland cement CEM I 52,5R and by adding Degussa P25 TiO_2 nanoparticles, with constant, 0.5 water : dry powder ratio. The amount of TiO_2

nanoparticles in the mixtures was: 0% (control sample), 1%, 2%, 3%, 3,6%, 4%, 5%, 6%, 10% and 12% (percent relative to the amount of dry cement).

On fresh mixtures, the setting time was determined, according to EN 196-3. At the same time, 130x85x10mm specimens were produced. The test specimens were conditioned for 24 hours in molds, at 20°C and 90% RH, away from any source of light. After demolding, the specimens were completely immersed in water at a temperature of 20°C, without light, for 27 days.

After ageing, the following test were conducted on the specimens: bulk density (according to EN 1015-10), absolute density (according to EN 1907-6), porosity (measured as ratio between the difference in absolute density and apparent density to absolute density), water absorption, capillary water absorption (according to EN 1015-18), and the degree of whiteness by direct measurement with a portable WSB-1 Leucometer (measured as the fraction of absorbed light directed on to the surface to be analyzed, after the samples were exposed to natural light and in laboratory conditions). The measurement of the white degree was initially performed without exposure of the specimens to the action of UV radiation, after which they were exposed 24 hours to the action of UV rays and the measurement was repeated. Exposure to UV action was carried out in an enclosure with 4 UVA bulbs (Figure 1).

Fig.1. UV testing device

Prismatic specimens with an exposed surface area of 0.085 m^2 were made to determine the water absorption at the surface. The proportion of TiO_2 nanoparticles introduced into the cementitious material was 1% (P2), 2% (P3), 3% (P4), 3.6% (P5), 4% (P6), 5% (P7), 6% (P8) and 10% (P8), percentages relative to the amount of cement. We also prepared a control sample, P1, cementitious composition without the addition of TiO_2 nanoparticles. For all cases, the ratio of water/dry powder material 0.5 was kept constant, where dry powder material represented the sum of the amounts of cement and TiO_2 nanoparticles. The test pieces were matured (28 days after pouring) and dried to a constant mass, after which they were exposed with an inclination of 10° from the vertical. From a distance of 30 cm, 5 ml of distilled water was sprayed every 2 minutes until a cumulative water volume of 50 ml was reached. After each test step (i.e. after each spray of 5 ml distilled water), the test pieces were weighed and the surface water absorption was determined. The test specimens were dried at constant mass, exposed to UV radiation for 1h, repeated testing, then dried again at constant mass, exposed to UV for 24 h and tested. The exposure was carried out in a test device with UV lamps with wavelength in the field of UVA and luminous intensity of 405 lux. (Figure 1).

Surface water absorption (Q) was calculated (Eq.1), as follows:

$$Q_t=(m_t-m_0)/A \ (kg/m^2), \quad (1)$$

where:

m_t - sample mass at time t (2, 4, 6, 8, 10, 12, 14, 16, 18, 20 minutes) from the start of the spraying, which corresponds to specific volumes (5, 10, 15, 20, 25, 30, 35, 40, 45, 50 ml) of sprayed distilled water;

m_0 - initial mass of the dry specimen at constant mass;

A - exposed surface of the specimen.

3. RESULTS AND DISCUTION

The main objective of this study was to analyze the influence of the presence of titanium dioxide (TiO_2) nanoparticles on the physico-mechanical properties of cementitious composites. Experimental results are presented in Figures 2…15.

From the point of view of the influence of TiO_2 nanoparticles on the setting time, results have shown that:

- with the increase in the amount of TiO_2 nanoparticles in the mixture, the setting time, both initial and final, decreases (Figure 2). The same evolution of the recorded setting times can be defined by a Grade 2 polynomial function (Figure. 3), with a sufficiently high precision coefficient (R_2 = 0.9379, respectively 0.9691) to be used for the assessment of the initial time, respectively of the final setting time for mixtures produced with other content of TiO_2 nanoparticles, under the same mentioned conditions;
- the greater the addition of nanoparticles, the smaller the difference between the beginning and the end of the setting time, which means a strong influence of TiO_2 nanoparticles on the setting time of the cementitious composites. The influence of the addition of nanoparticles on the setting time is consistent with some specifications in the literature and probably occurs as a result of the acceleration of the hydration-hydrolysis processes and the operation of the nanoparticles as cores of formation and growth of the network of hydration – hydrolysis products specific to the cement outlet.

As for the apparent density in hardened state of the cementitious composites (Figure 4), it is noted that it does not vary in proportion to the content of TiO_2 nanoparticles. However, a constant range of high values is recorded in the concentration range 3.6% - 5%, after which a constant trend of decrease of the parameter is observed. These results are correlated with the reports in the literature. Experimental results indicate that the absolute density of the cementitious materials with the addition of TiO_2 nanoparticles does not vary in proportion to the content of nanoparticles (Figure 5).

Porosity (Figure 6) was determined by calculation based on experimentally obtained values for apparent density and absolute density, for each mixture. Thus, it was observed that the lowest porosity value was obtained for a content of TiO_2 nanoparticles of 3.6% and the highest value was obtained when 6% TiO_2 nanoparticles were added to the mixture. No function could be identified indicating the variation of porosity depending on the amount of TiO_2 nanoparticles introduced into the mixture.

When determining the water absorption it was observed that the lowest value of the water absorption percentage is given by the addition of 4% TiO_2 nanoparticles relative to the quantity of cement, and the highest value of the water absorption percentage is given by the addition of 12% TiO_2 nanoparticles (Figure 8). The variation of water absorption in relation to the amount of nanoparticles introduced into the cementitious matrix can be expressed by a polynomial function of order 4 (Figure 7).

Similarly, capillary water absorption (Figure 9) presents a minimum for the situation in which the addition of TiO_2 nanoparticles was 4% and the maximum for the situation in which the addition of nanoparticles is quantitatively 10%.

Regarding the white degree, it was observed that for the same cementitious mixtures with the addition of TiO_2 nanoparticles, this parameter increased for all analyzed cases, after 24 hours of UV exposure, compared to the control sample (Figure 10). However, it is noted that in the range 1-4% TiO_2 the variation of the white degree is significantly higher than in the case of mixtures with higher content of nanoparticles.

Thus, a maximum increase in the degree of white is recorded, both as difference between the initial and final values and as percentage change relative to the initial value, for the mixture containing 2% TiO_2.

Mixtures produced with 1%, 3%, 3.6% and 4% TiO_2 nanoparticles had all increases in the degree of white, the difference between the final values and the initial values being over 0.4, as opposed to those with much higher content of nanoparticles (5%, 6%, 10%, 12%) for which there were increases in the degree of white by only 0.14…0.31 from the initial value.

The same increase in the degree of white (Figure 11) represents an image of the photoactivation activity.

Variation of the degree of white relative to the initial value (Figure 12) represents a measure of the efficiency of the addition of nanoparticles on this parameter. Thus, it can be seen that additions of 1…4% TiO_2 provide a minimum 50% increase in the degree of white by photoactivation, and larger additions of nanoparticles, are not effective, by generating unfavorable performances to the evolution of this parameter.

With regard to surface water absorption (Figures 13…15), it can be observed that with the increase in the amount of water sprayed, it increases continuously and steadily for all cases analyzed. Thus, this increase can be expressed mathematically by equations of first degree of the form ax+b. It can be observed that the maximum water absorption is, in the case of P8 composition with 6% TiO_2, for all situations of the amount of water sprayed, both in case of non-exposure to UV radiation and in case of exposure for 1 h to UV radiation. In the case of samples exposed 1 + 24 h to UV action the maximum water absorption is reached, initially, in the case of P5 composition (3.6% TiO_2). This is followed by the P8 composition (6% TiO_2). With the increase in the amount of water sprayed, an increase in water absorption is observed for all compositions in the range P2…P8 (1% TiO_2…6% TiO_2). The composition of P9 (10% TiO_2) causes the reduction of water absorption on the surface, so we can say that increasing the amount of TiO_2 over 6% causes the reduction of water absorption on the surface. The control sample (P1) shows a much reduced evolution of the water absorption process on the surface, compared to the composite samples with nanoparticles content, both in the case of specimens not exposed to UV radiation and in the case of their exposure for 1h and for 1 + 24 h. In general, it can be said that, at the beginning of the test, the evolution of water absorption on the surface from one spray to the next, is more strongly influenced by the amount of TiO_2. As the amount of water sprayed increases, the absorption process on the surface stabilizes, decreasing the percentage of water added by each spray.

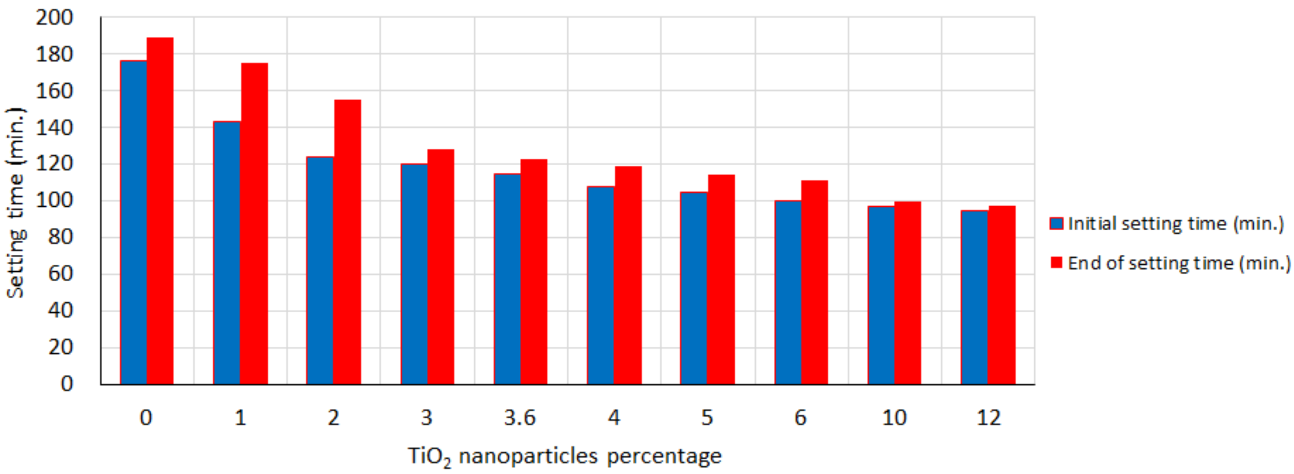

Fig.2. Setting time values of the cementitious mixtures with TiO_2 nanoparticles addition

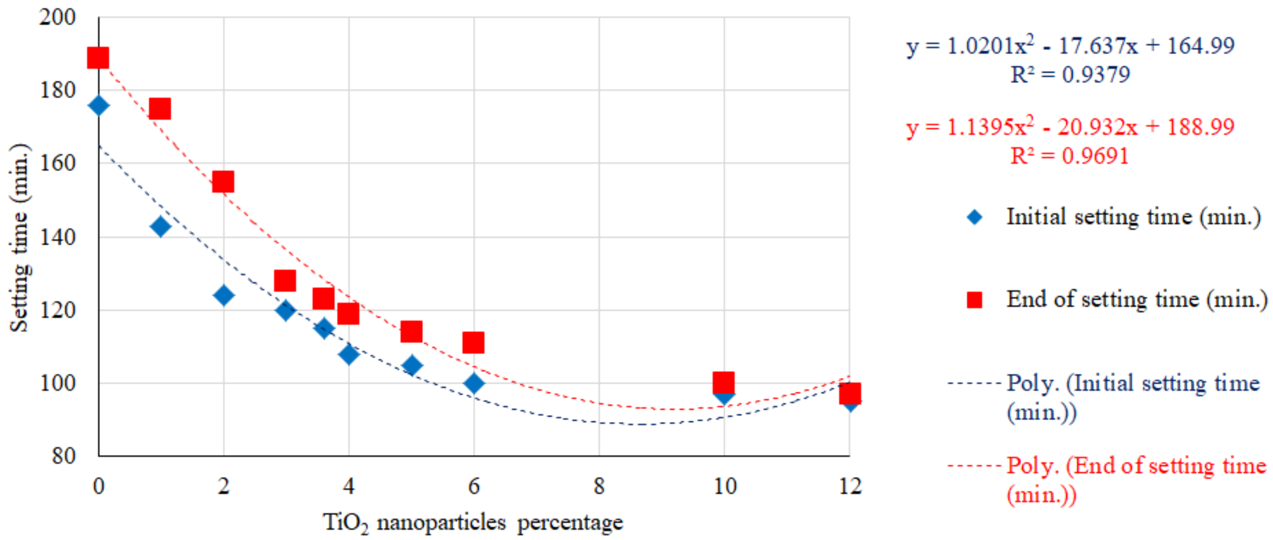

Fig.3. Setting time polynomial function

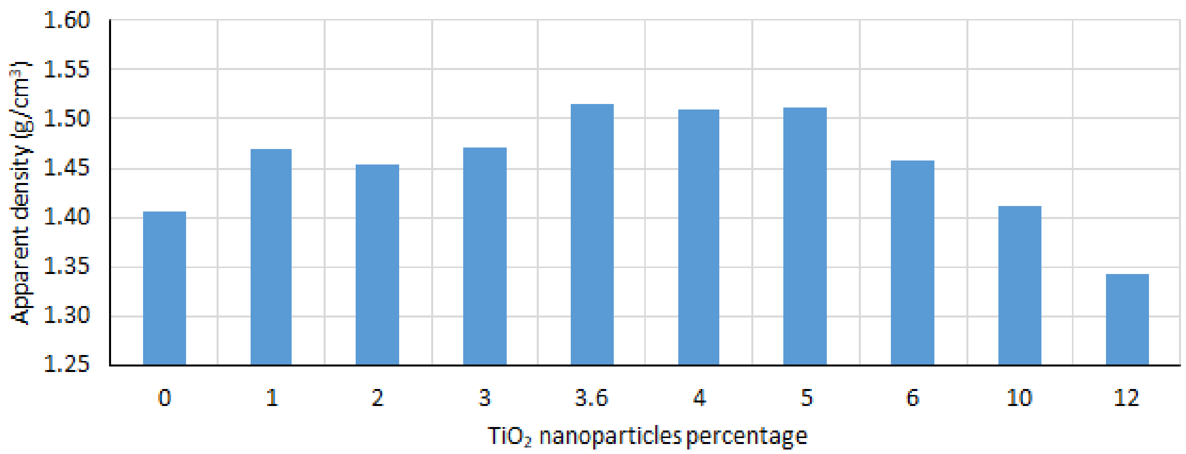

Fig.4. Apparent density of the cementitious composites with TiO_2 nanoparticles addition

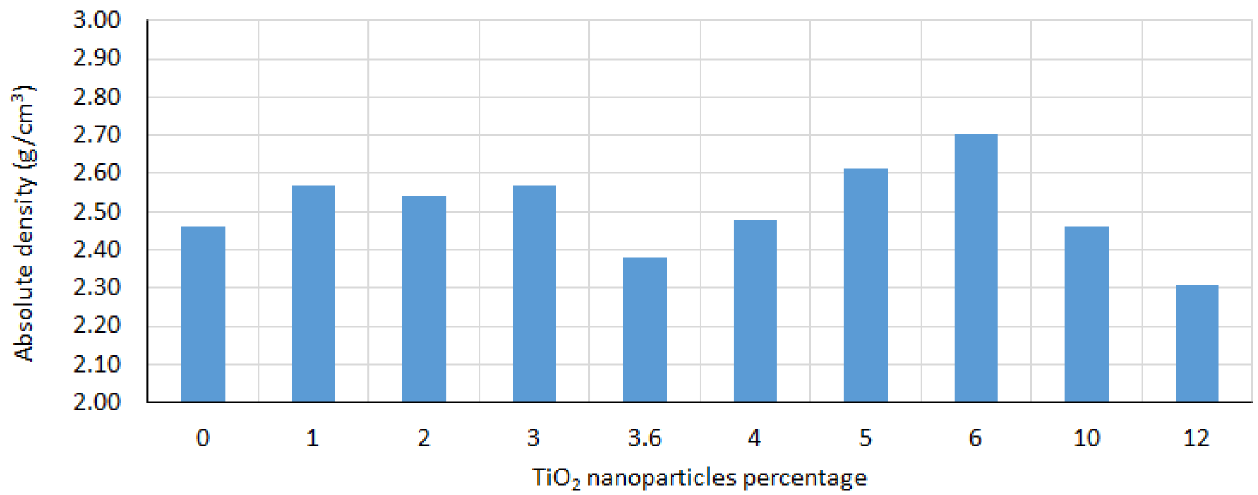

Fig.5. Absolute density of the cementitious composites with TiO_2 nanoparticles addition

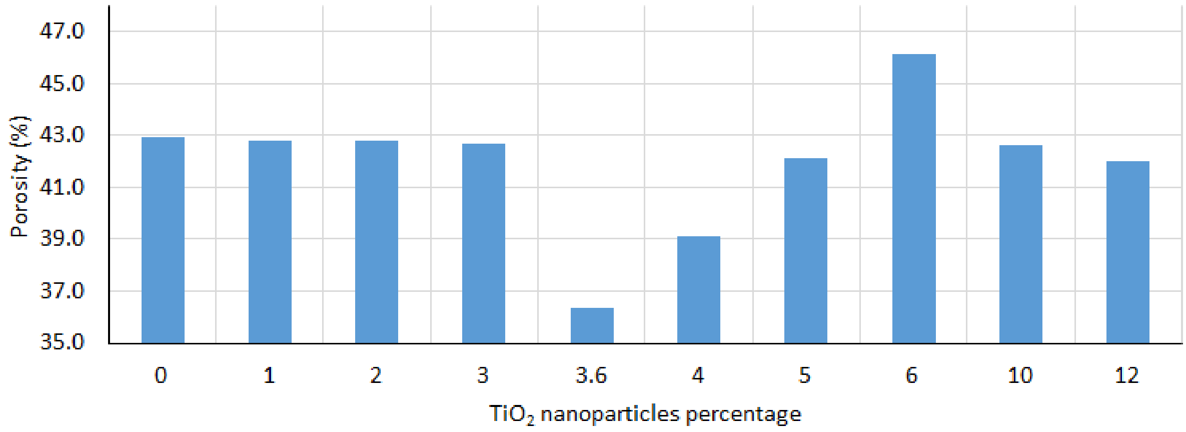

Fig.6. Porosity of the cementitious composites with TiO_2 nanoparticles addition

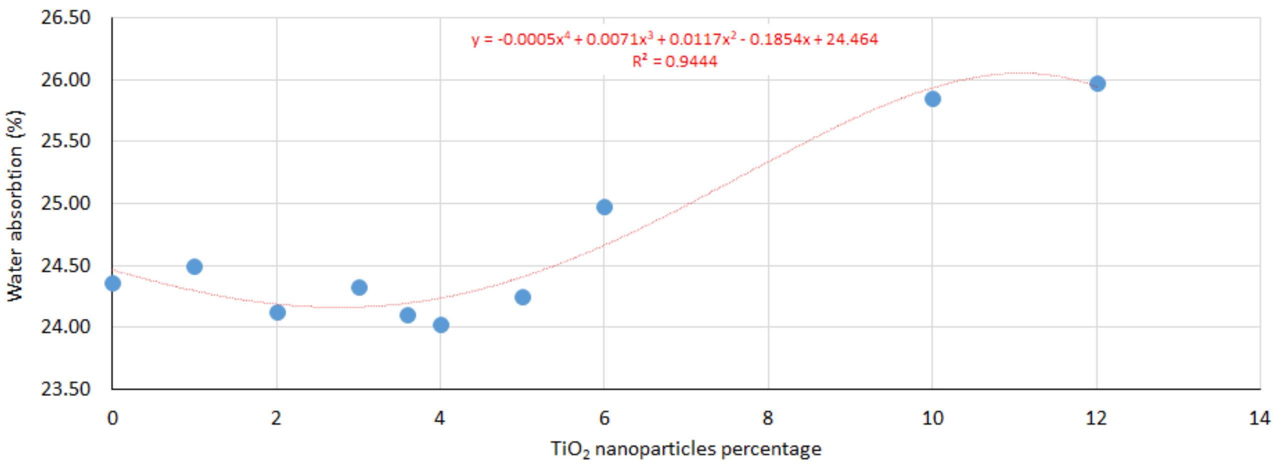

Fig.7. Water absorption polynomial function

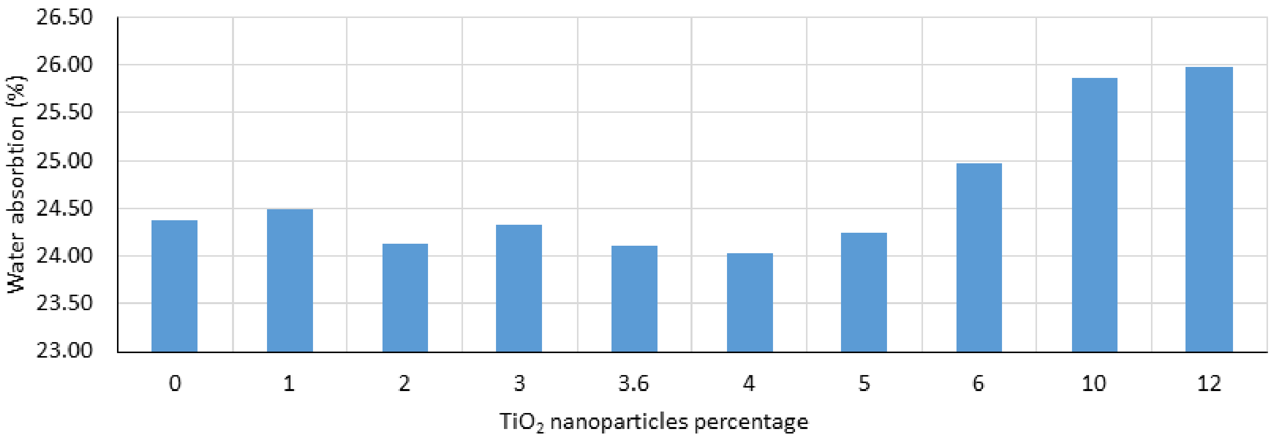

Fig.8. Water absorption of the cementitious composites with TiO_2 nanoparticles addition

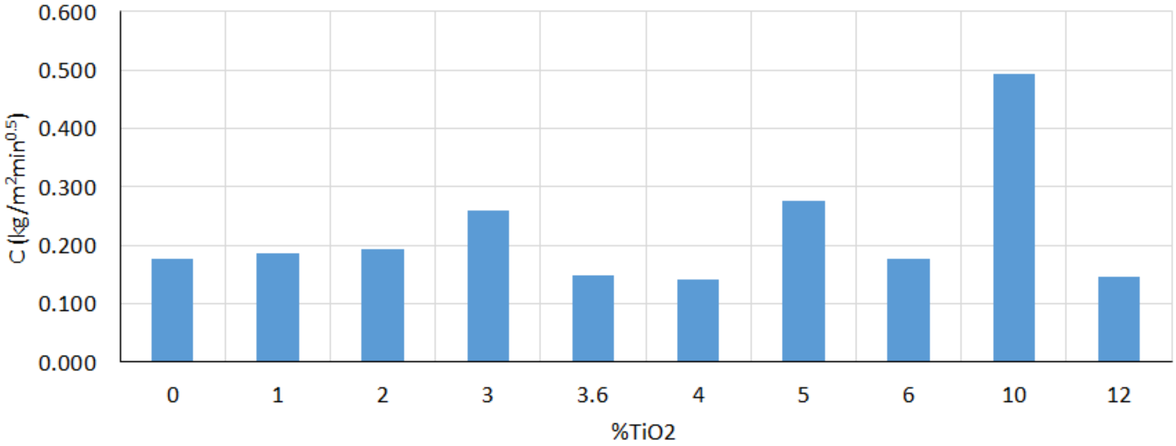

Fig.9. Capillary water absorption of the cementitious composites with TiO_2 nanoparticles addition

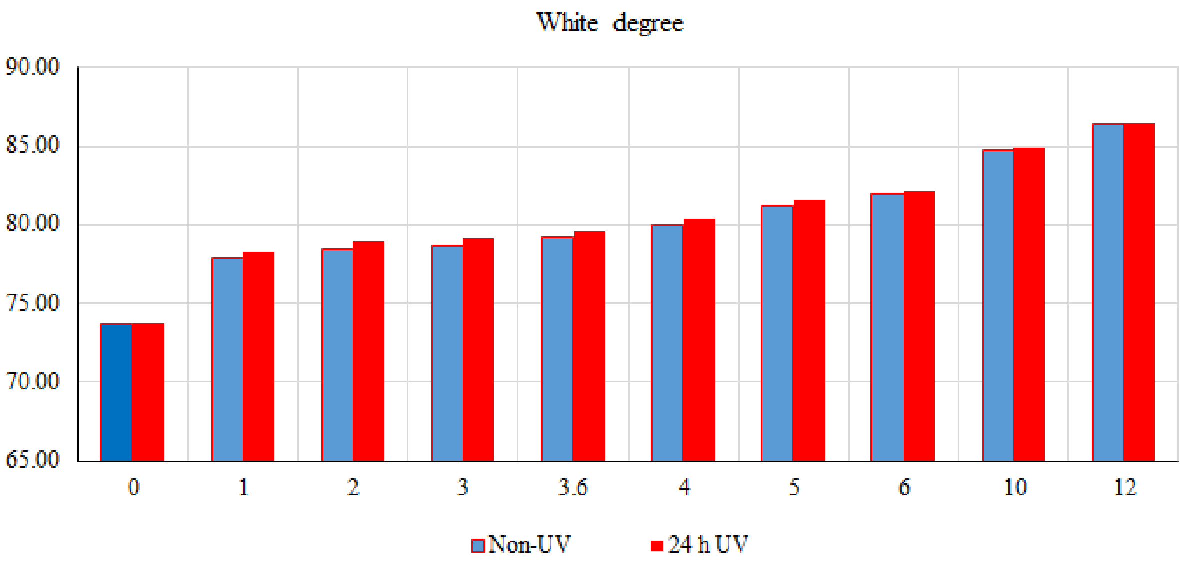

Fig.10. White degree of the cementitious composites with TiO_2 nanoparticles addition

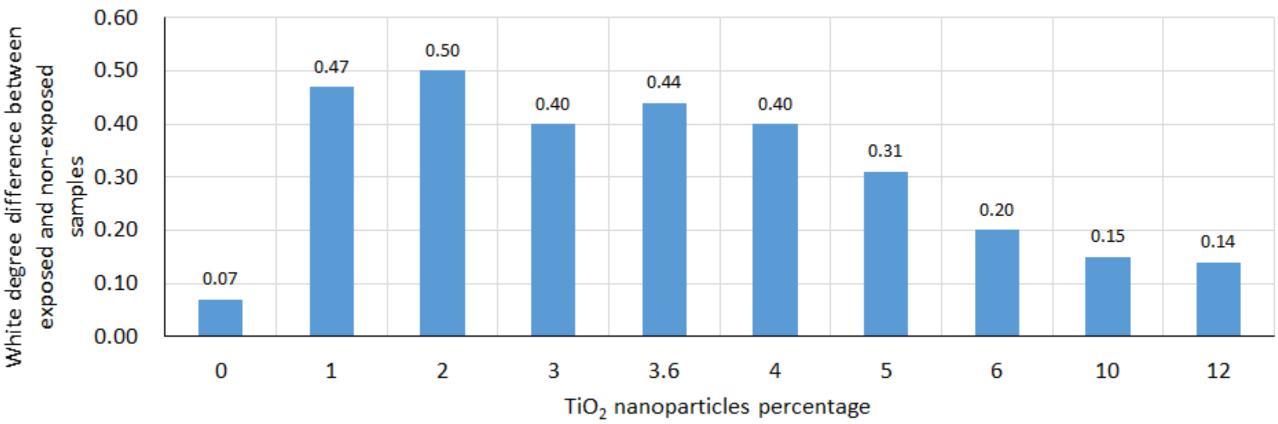

Fig.11. Difference between exposed and unexposed samples to UV action

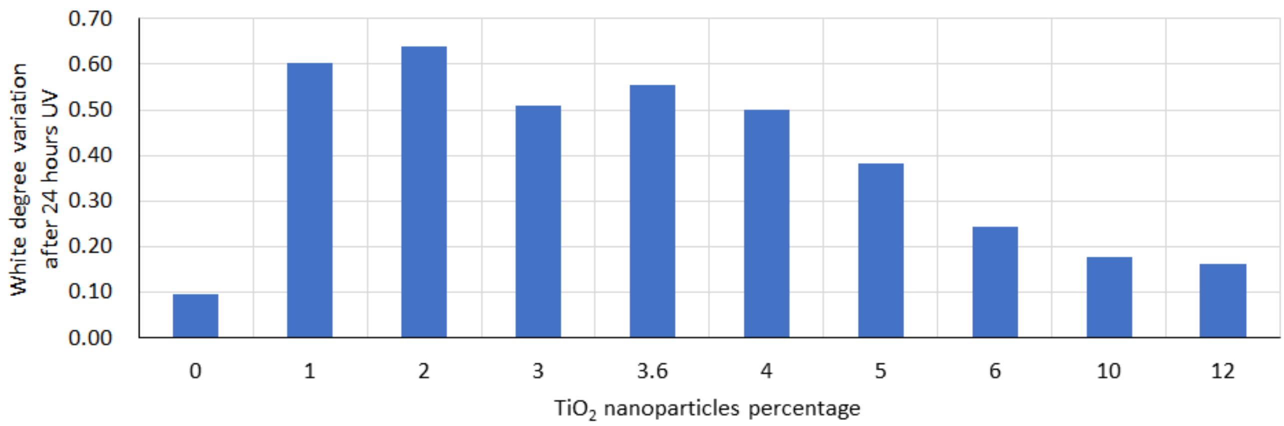

Fig.12. White degree variation after 24 hours of UV exposure

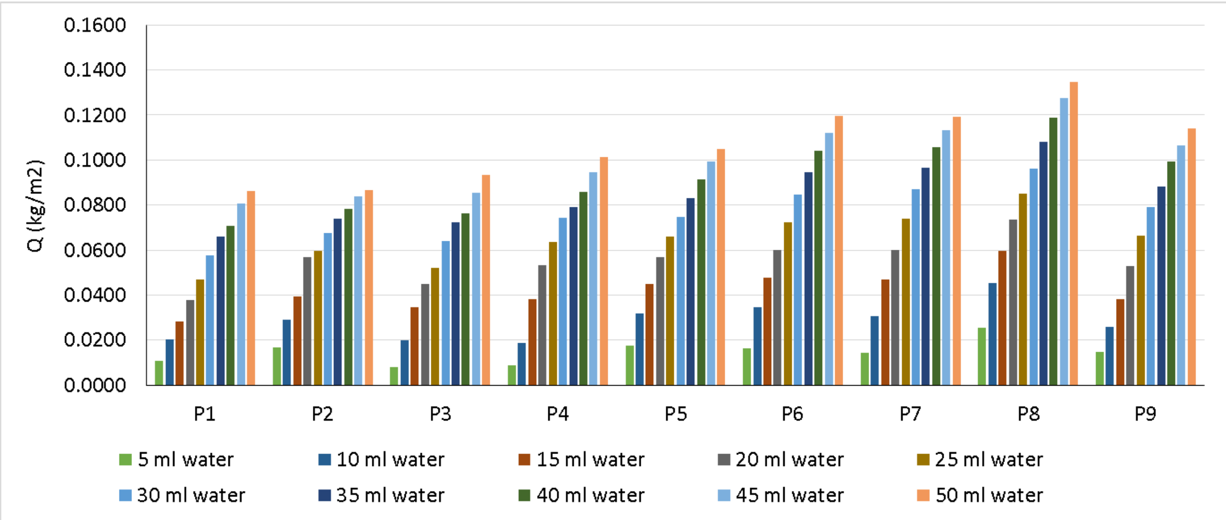

Fig.13. Surface water absorption on samples not exposed to UV

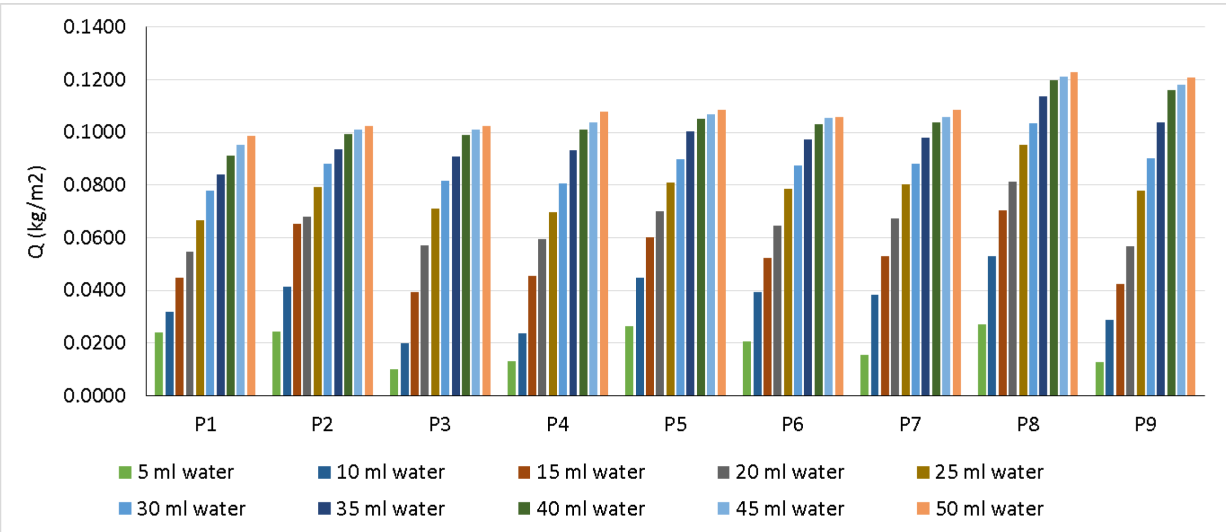

Fig.14. Surface water absorption on samples exposed 1 h to UV

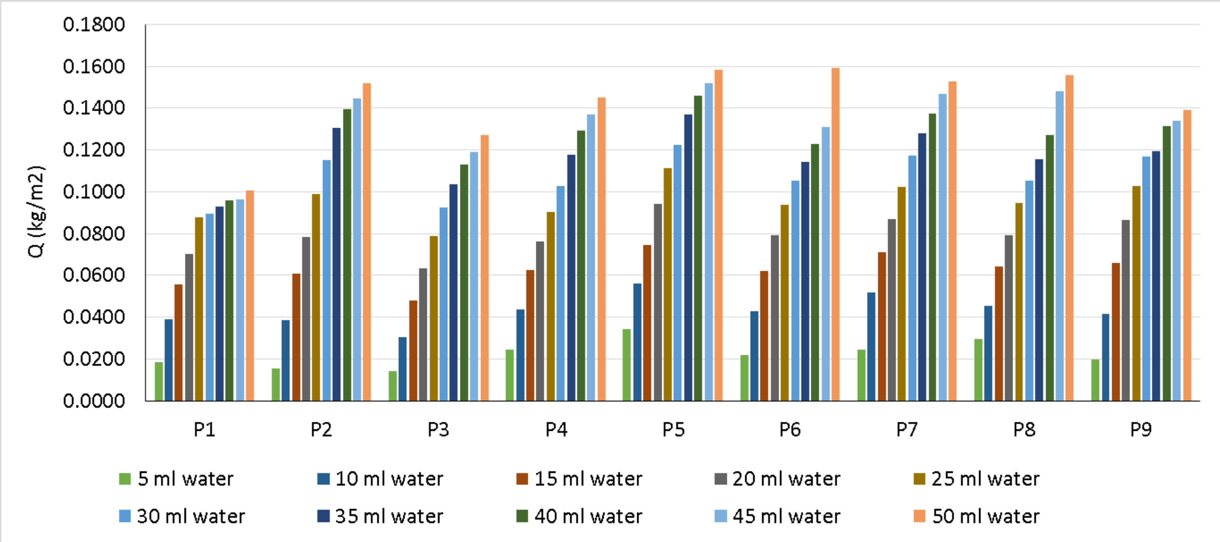

Fig.15. Surface water absorption on samples exposed 1+24 h to UV

4. CONCLUSIONS

The experimental results obtained on the above presented cementitious composites with TiO_2 nanoparticles addition showed the following:

- with the increase in the amount of TiO_2 nanoparticles in the cementitious mixture, the setting time, both initial and final, decreases;
- as for the apparent density in hardened state of the cementitious composites, it is noted that it does not vary in proportion to the content of TiO_2 nanoparticles;
- the absolute density does not vary in proportion to the content of nanoparticles;
- porosity does not vary in proportion to the content of TiO_2 nanoparticles in the mixture;
- the variation of water absorption in relation to the amount of nanoparticles in the matrix can be expressed by a polynomial 4th degree function;
- regarding the white degree, it was observed that for the same mixtures with TiO_2 nanoparticles addition, this parameter increased after exposure to UV for 24 hours, for all analyzed samples when comparing to the control sample. The white degree variation is a measure of the efficiency of the addition of nanoparticles on this parameter.
- water absorption at the surface increases continuously and steadily for all cases analyzed, with increasing amount of water sprayed. The P8 sample, with the addition of 6% TiO_2 nanoparticles, relative to the amount of cement has the most balanced and favorable behavior in terms of the evolution of the phenomenon, the kinetics of the surface water absorption process and the efficiency of the presence of nanoparticles, in relation to the control sample.

It is essential to identify the optimal concentration range of nanoparticles, so as to achieve an optimal benefit-cost ratio, namely maximum efficiency, photoactivation, while preserving the other physico-mechanical properties of the cementitious material, who wants to induce the quality of self-cleaning, depending on the destination of use, climate, degree and duration of sunshine at the same time with a reasonable cost in relation to the benefits. This conclusion is consistent with relevant specifications from the literature (Folli 2010; Rashad, 2015).

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