

This study has established the impact of a nano-TiO₂ P25 modifier and a nanocomposite based on titanium dioxide, doped with sulfur and carbon dioxide (TiO₂/S, C), on the photocatalytic, mechanical properties and the structural formation of cement mortars. The paper reports the results of the particle size distribution of the Portland composite cement and the TiO₂ nano additives; a comprehensive assessment of the particle size distribution has been performed both in terms of volume and specific surface. It has been proven that the TiO₂/S, C nanocomposite is characterized by the extremely high surface activity, which determines the photocatalytic properties of the surface of cement mortars. The comparison of the mechanical properties of cement mortars modified by titanium dioxide nano additives has been carried out.

An experimental study has confirmed the improved photocatalytic properties of the cement mortar surface in the visible spectrum through the doping of the nano-sized titanium dioxide with carbon and sulfur. A combination of the TiO₂ nano additives and the superplasticizers of polycarboxylate type leads to the increased strength of the modified samples in proportion to a hardening age. Given the high surface activity of the TiO₂/S, C nanocomposite's particles, the cement paste hydration products deposit at their surface, thereby forming such conglomerates with them that seal the microstructure of the cement matrix. It has been shown that using a nanocomposite based on the modified titanium dioxide decreases the indicators of free energy while the surface of the cement mortar acquires hydrophobic properties, which contributes to the processes of self-cleaning. Thus, there is a reason to argue about the feasibility of using the TiO₂/S, C nanocomposite to improve the photocatalytic, self-cleaning, mechanical, and hydrophobic properties of cement mortars

Keywords: *nanocomposite, titanium dioxide, cement mortar, photocatalysis, hydrophobicity, free energy*

UDC 666.971

DOI: 10.15587/1729-4061.2020.210218

THE EFFECT OF SULFUR- AND CARBON-CODOPED TiO₂ NANOCOMPOSITE ON THE PHOTOCATALYTIC AND MECHANICAL PROPERTIES OF CEMENT MORTARS

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Received date 15.06.2020

Accepted date 17.08.2020

Published date 31.08.2020

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1. Introduction

The development of modern technologies in the construction industry gives rise to the new format of housing – multi-comfortable houses. The “Active House” concept of such buildings predetermines the need for a synergic combination of key factors such as energy efficiency, comfort, and healthy living conditions. At present, the development of nanotechnologies that can be used for designing multifunc-

tional materials of the new generation [1–4] is an important task and priority in construction. Among these materials are the nanomodified cement mortars with the photocatalytic and hydrophobic properties. Multifunctional cement composites containing the nano-sized titanium dioxide ensure the self-purifying properties and the ability to clean air from organic pollutants. This makes it possible to build smart functional buildings that provide the effect of self-cleaning, as well as the antimicrobial properties, and help clean the air

and environment. Such a product has been also widely used for external application when finishing road tunnels and buildings in areas with contaminated air [5–9].

Currently, the actual application scope of the photocatalysis process involves the disinfection and deodorization of air inside the premises. The high oxidative and reducing capabilities of nano-TiO₂ make it one of the most effective photocatalysts for the neutralization of organic pollutants and aromatic compounds, conversion of solar energy, creation of self-cleaning surfaces [10, 11]. The photocatalytic nano-sized titanium dioxide has the biocide properties confirmed for a series of viruses and cyanobacterium [12]. This focus necessitates research on the possibility of using photocatalytic technology to reduce the level of pollutants in the air. The process of photocatalysis has already been used to clean water and air from pollutants, as well as to create self-cleaning surfaces with hydrophobic properties.

Given the compatibility with various kinds of building materials without deterioration of their operational characteristics, the most widely used component in the photocatalytic structural materials is the nano-sized titanium dioxide. Considering the need to develop modern multifunctional building materials, it is a relevant task to study the influence of the nano-TiO₂-based modifiers on the photocatalytic, hydrophobic, and antibacterial properties of finishing solutions based on multi-component cement. Modern cement-sand mortars are used for exterior and interior plasters that do not require coating with finishing materials. The development of such cement mortars makes it possible to create self-cleaning surfaces with improved operational and aesthetic characteristics. This approach also makes it possible to solve a series of important environmental issues. In this case, there is a need for an in-depth study of the impact of nano-TiO₂ on the photocatalytic and mechanical properties of cement mortars based on them. However, the photocatalytic properties of nano-TiO₂ are manifested under the exposure to UV radiation. At the same time, finishing solutions for internal works are more subject to the effect of light in the visible range, which limits the effectiveness of the use of cement mortars with the addition of nano-TiO₂ in the premises.

2. Literature review and problem statement

Finishing solutions are typically used for internal and external works in buildings. Papers [13, 14] report the results of studying cement mortars based on low-energy multi-component and composite cement. They show the possibility of creating decorative multi-component cement through the systematic combination of the Portland cement clinker, mineral additives of various substances, and fillers of light tones for finishing operations. In this case, the issues of the impact of TiO₂ nano additives on the photocatalytic and mechanical properties of plasters for internal premises remained unsolved. The cause of the low photocatalytic activity of the surface of cement mortars is the insufficient intensity of UV radiation indoors. In addition, the highly-dispersed nano additives increase the water need for soluble mixtures, which leads to an increase in shrinkage deformations and crack formation. The option to overcome these problems may be the use of special TiO₂-based nanocomposites that ensure the photocatalytic properties in the visible range of light. The combination of ultra disperse nano additives with the hyperplasticizers of polycarboxylate type can im-

prove the mechanical properties of cement mortars based on multi-component cementing systems [15–18].

Experimental study [19] proves the effectiveness of the application of nano-sized additives of TiO₂ in order to increase the photocatalytic activity of building materials' surfaces. Currently, there are many modifications of titanium dioxide, designed to improve its technical characteristics and properties. The results of the study show that titanium dioxide exists in nature in three crystalline modifications: anatase, brookite, and rutile. Anatase and rutile can be easily synthesized in a laboratory, while brookite is almost impossible to synthesize artificially. Therefore, for applied purposes, the TiO₂ of rutile and anatase modifications are used. The authors of [20] show that the highest photocatalytic activity is demonstrated by titanium dioxide in a combination of anatase (15–25 nm) and rutile (45–60 nm) crystalline phases.

The nano-sized photocatalysts of titanium dioxide with a tetragonal crystalline structure show the photocatalytic properties. Titanium dioxide has high effectiveness of removing volatile organic compounds with concentrations of 0.01–10 ppmv [21]. This has a positive effect on indoor air purification. Paper [22] found that pores in the plaster structure above 10 μm work as macropores and the pores between 10 and 0.1 μm are treated as micropores and those below 0.1 μm – as nanopores. It was established that the photocatalytic activity is contributed to by the higher porosity. At the same time, the prevalence of nanopores is an obstacle to the diffusion of pollutants into the cement matrix. In this case, one should take into consideration the loss of the mechanical strength of the cement mortar when porosity grows. Based on comparing the effect of photocatalytic activity and the loss of the mechanical strength of cement mortars, it was found that the optimal amount of a titanium dioxide nano additive is 1.0–2.0 wt. % of the binder.

Doping the titanium dioxide nanopowder with nonmetals makes it possible to increase the photocatalytic property of the surface in the visible range of the spectrum. Such nanocomposites are effective modern photocatalysts that can be used for the photocatalytic processes of oxidation of harmful substances in indoor areas [23]. A composition for obtaining the powder of titanium (IV) oxide – S-TiO₂, sulfur-doped, with a high specific surface was developed [24]. Based on the research, it was determined that the modification of TiO₂ particles with sulfur proceeds according to the following scheme. Sulfur-containing particles with a diameter of ~10 nm are segregated at the surface of anatase crystals with a diameter of ~20 nm. The formed globules create the nanostructured spheres with an average diameter of about 1.0 μm. To determine the limit of absorption of the synthesized nanopowder of S-TiO₂, the UV absorption spectra were acquired in the range of waves 200–800 nm. According to the spectrum, the S-TiO₂ powder absorption limit is equal to 420 nm, that is, the edge of the S-TiO₂ absorption is shifted to a visible range. A study was conducted [25] to apply an electron paramagnetic resonance method to prove that such a material effectively generates free radicals when exposed to radiation in the visible range.

Paper [26] describes the processes of doping titanium dioxide with carbon and sulfur and gives the characteristics of the nanopowders modified by them. Particular attention should be paid to TiO₂, doped with sulfur and carbon, which shows a much higher photocatalytic activity in the visible spectrum, compared to the commercially available TiO₂ nanopowders,

the type of P25. It was shown [27] that $\text{TiO}_2/\text{S, C}$ has an absorption edge of 650 nm, while conventional TiO_2 nanopowder operates only in the UV spectrum (up to 350 nm). However, the impact of the nano-sized titanium dioxide on the surface activity of cement mortars remains to be studied.

Another important characteristic when evaluating surface hydrophobicity is the value of the surface free energy (SFE). The advantages of using nano-sized particles imply that the high value of the specific area of their surface leads to an increase in the activity of surface reactions. Free surface energy (surface tension) is also a key parameter when evaluating the physical and chemical characteristics of solid surfaces. SFE is one of the thermodynamic quantities describing the equilibrium of atoms in the surface layers of materials. Free energy represents the imbalance of intermolecular interactions present at the phase boundary of two different environments. The decrease in SFE characterizes an increase in the surface hydrophobicity and, accordingly, its corrosion and frost resistance [28].

The feasibility of developing the nanomodified multifunctional cement mortars with the photocatalytic and hydrophobic properties is predetermined by the possibility of their subsequent application in the premises in order to create a microclimate favorable for humans.

3. The aim and objectives of the study

The aim of this work is to study the impact of the $\text{TiO}_2/\text{S, C}$ nanocomposite on the photocatalytic, hydrophobic, and mechanical properties of cement mortars in order to obtain the effect of surface self-cleaning in the interiors of buildings and structures in a visible spectrum of light.

To accomplish the aim, the following tasks have been set:

- to investigate the impact of the TiO_2 P25 and $\text{TiO}_2/\text{S, C}$ nanomodifiers on the particle size distribution in a cement system and the processes of structural formation;
- to investigate the photocatalytic activity of the nano- TiO_2 P25 modifier and the $\text{TiO}_2/\text{S, C}$ nanocomposite, to determine their impact on the mortars strength;
- to investigate the dependence of the contact angle of liquids with the surface when applying the TiO_2 P25 and $\text{TiO}_2/\text{S, C}$ nanomodifiers;
- to investigate the indicators of the free energy of surfaces of the modified compositions and the impact of a given indicator on the hydrophobic properties of cement mortars.

4. Materials and methods to study the nanomodified photocatalytic cement mortars with hydrophobic properties

4.1. The examined materials and equipment used in the experiment

Our study involved the compositional Portland cement CEM II/B-M (S-P-L) 32.5R (produced at PJSC “Ivano-Frankivsk cement”, Ukraine) based on the Portland cement clinker of the normalized mineralogical composition (wt. %: C_3S – 61.8; C_2S – 14.25; C_3A – 7.20; C_4AF – 11.85) and 35 wt. % of such basic ingredients as granulated blast furnace slag (S), natural zeolite (P), and limestone (L). The apparent density of the Portland cement CEM II/B-M is 3.0 g/cm^3 , a specific surface (by Blaine) is $380 \text{ m}^2/\text{kg}$. The

fine aggregate used was natural quartz sand (Velyko-Glibovytske deposit, Ukraine) with a module size of $M=1.24$. Cement-sand mortar with the rated composition (the ratio of cement:sand=1:3) with a water-cement ratio of 0.50 was used as control. The applied plasticizing additive was a highly reducing superplasticizer of the new generation, based on polycarboxylate ether (PSE) with the nanodesigned chains of the Master Glenium Ace 430 type (BASF, Germany).

The TiO_2 P25 nanopowder of titanium dioxide (Evonik Industries, Germany) was used as a modifier; it consisted of 85 % of anatase and 15 % of rutile, with a specific surface area of $50 \pm 10 \text{ m}^2/\text{kg}$, whose particle size distribution for the fractions of 20, 25, and 30 μm is 15, 60, and 25 vol. %, respectively [29]. Titanium dioxide, doped with sulfur and carbon, $\text{TiO}_2/\text{S, C}$ (Ukraine) was also used as a nanomodifier; it consisted of 97 % of anatase. In this case, the particle size was 10–30 nm (the sulfur content (S) is 0.45 %; carbon (C) – 2.38 %). The specific surface area of the nanocomposite $\text{TiO}_2/\text{S, C}$ is $110 \pm 10 \text{ m}^2/\text{kg}$.

The colorant Rodamine B (Rhodamine 610), $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$, (Ukraine) was used to determine the level of photocatalytic activity.

The VEGA3 TESCAN microscope (Czech Republic) was used to acquire images using a scanning electron microscopy method. To determine the phase composition of the mortar, we used X-ray analysis (the diffractometer DRON-3, Russia). The photocatalytic performance of samples was determined by spectrometry using the VLS-1 spectrometer (Visual Light Spectrometer) (Japan). Theta Flex tensiometer (Biolin Scientific, Sweden) was applied to determine the surface hydrophobicity.

4.2. Procedure for determining the indicators of samples' properties

The physical and mechanical properties of the nanomodified mortars with the photocatalytic and hydrophobic properties were determined in accordance with the acting standards and generally accepted procedures.

The particle size distribution in cement systems was determined using the laser analyzer Mastersizer 3000 (Malvern Panalytical, UK). The specific surface of cement and titanium dioxide was determined by the method of air permeability according to EN 196-6. Based on the results of laser granulometry, the differential coefficient of particle size distribution by specific surface area, K_{isa} , was calculated. This coefficient makes it possible to estimate distribution of the SCMs particle sizes over a specific surface area, which makes it possible to determine a degree of additional active interphase surface of SCMs of cementitious materials. A given coefficient is determined as a product of the ratio A/V (the surface area of particles to their volume, μm^{-1}) by the content of fractions of the material by volume based on the data of laser granulometry, according to the following formula:

$$K_{isa} = A/V \cdot \omega_i [\mu\text{m}^{-1} \cdot \text{vol. \%}], \quad (1)$$

where ω_i is the content of the i -th fraction, vol. %.

To determine the strength of the mortar, the sample prisms from the cement-sand mortar, $20 \times 20 \times 80 \text{ mm}$, and the sample cubes, the size of $20 \times 20 \times 20 \text{ mm}$, at the C:S ratio 1:3 (W/C=0.50) were prepared. Samples in the molds were aged for 24 hours while maintaining the temperature ($20 \pm 2 \text{ }^\circ\text{C}$) and moisture (90-100 % RH) modes. After

disbanding and labeling, the samples were placed in the storage exicator before testing in 7, 28, and 90 days.

To determine the photocatalytic activity of the surfaces, tablet shape samples of the cement-sand mortar, with a diameter of 32 mm and a thickness of 5 mm were prepared. The photocatalytic activity of the samples' surfaces was studied under exposure to a diode laser (maximum power, 700 mW) with a wavelength of 532 nm (green light) over 2 hours, as a source alternative to UV. The radiation capacity density in the sample plane was 18 mW/cm².

Determining and controlling the optical characteristics of the colorant for transmission during degradation were carried out using a low-intensity (maximum power, 400 mW) diode laser with a radiation wavelength of 445 nm (blue light) in 1 hour and after 2 hours of irradiation. The power density in the sample plane at a distance of 20 cm from the source of exposure was 15 mW/cm². The results were derived from the Thermano Spectrometer v.2.3 software.

The hydrophobicity of the surface was determined by the optical measurement of the angle of surface wetting. A drop of water in the volume of 2 microliters was applied onto the sample surface and recorded the image in 10 s. The tensiometer camera was used to determine the average angle of contact with the surface. The results were processed using the One Atention software.

When calculating the surface free energy, we additionally determined the contact angle of the α -Bromophthalene liquid using the tensiometer Theta Flex. The indicators of the surface free energy were calculated by an Owens, Wendt, Rabel and Kaelble (OWRK) method, which implies determining the disperse and polar components.

5. Results of studying the indicators of the nanomodified cement mortars with photocatalytic properties

5.1. Studying the particle size distribution in cement systems and the mechanical characteristics of cement mortars

A fundamental characteristic of cement systems, which largely determines their properties, is their granulometric composition, determined by the particle size distribution. The average diameter per volume $D[4, 3]$ for Portland cement CEM II/B-M is 26.3 μm , with the average diameter per specific surface $D[3, 2]$ corresponds to 4.02 μm . For the Portland cement CEM II/B-M, the residue on a sieve of 45 μm is 12.6 wt. %; at the same time, the specific surface corresponds to 497.0 m²/kg. That shows that the distributions of particles by volume and specific surface differ significantly; in this case, the particle size distribution by volume does not produce a true pattern relative to the chemical activity of cement particles. In this regard, the characteristic of the surface activity is to a greater extent reflected by the particle size distribution per specific surface. For the Portland cement CEM II/B-M, the maximum value of K_{isa} (4.96 $\mu\text{m}^{-1} \cdot \text{vol. \%}$) is achieved for a fraction of 0.275 μm ; for a fraction of 1.0 μm , a given coefficient is 4.59 $\mu\text{m}^{-1} \cdot \text{vol. \%}$; and for a fraction of 10 μm , it decreases by 3.5 times (Fig. 1, a).

With the particle size reduced to the nano range, the degree of dispersity $A/V=6/d$ increases dramatically. When the particle size is reduced from 1,000 to 100 and 10 nm, the A/V ratio increases by 10 and 100 times, respectively. Taking into consideration the volumetric content of particles, it is established for nano-TiO₂ that for particles the size of 20, 25, and 30 nm the K_{isa} coefficient is 4,500; 14,400; and 5,000 $\mu\text{m}^{-1} \cdot \text{vol. \%}$ (Fig. 1, b). In this case, the ratio of maximum values of K_{isa} coefficients for nano-TiO₂ and CEM II/B-M (respectively, at 25 and 243 nm) is 2,903 times. This indicates the extremely high value of the surface energy of ultra dispersed particles of nano-TiO₂ compared to the highly dispersed fraction of the Portland cement CEM II/B-M. At the same time, for the nanocomposite TiO₂/S, C, with the size of particles in the range of 10–30 nm, the degree of dispersity at $d_{cep}=20$ nm increases by 1.25 times, while the specific surface increases by another 2 times. In this case, the K_{isa} coefficient reaches a value of up to 20,000 $\mu\text{m}^{-1} \cdot \text{vol. \%}$, that is, the surface activity of the nanocomposite TiO₂/S, C is extremely high.

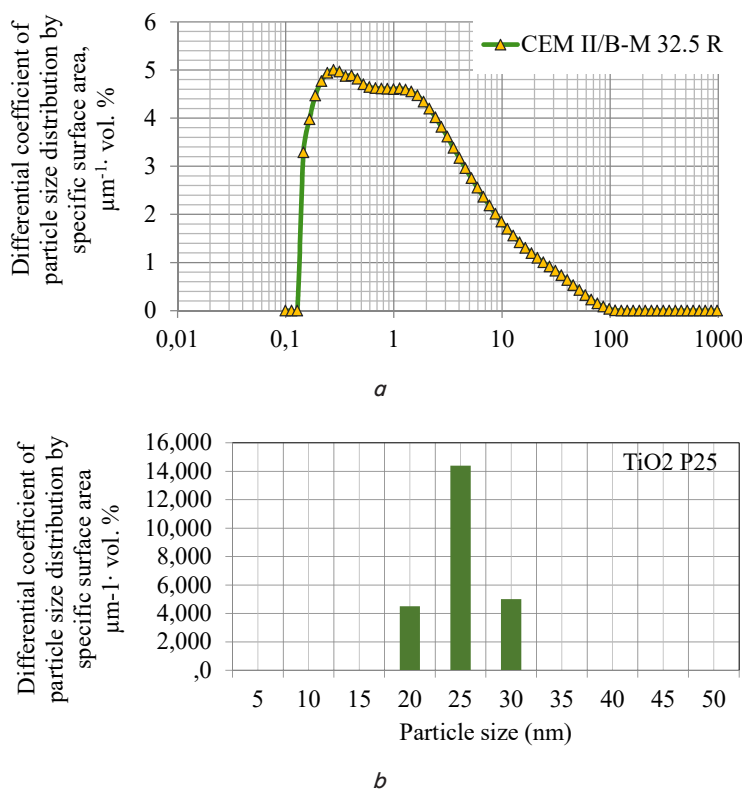


Fig. 1. Differential coefficient of particle size distribution per specific surface K_{isa} : a – CEM II/B-M; b – nano-TiO₂ P25

According to the results of determining a standard compressive strength, the mortar with a control composition corresponds to the strength class M100 ($R_{c28}=13.6$ MPa). Modifying a cement mortar with nano-TiO₂ and ethers of polycarboxylate ensures the growth of its early and standard strength. Thus, the compressive strength of the mortar with a content of 2.0 wt. % of TiO₂/S, C at 28 days, is 23.9 MPa, which is 75 % higher than the strength of the control composition mortar (Fig. 2, a). The flexural strength of such mortar at 28 days is 1.82 MPa. When modifying the mortar with an

additive with 2.0 % of TiO₂/S, C, the flexural strength increases by 44 % after 28 days (Fig. 2, *b*). The increased strength can be explained by the high surface activity of nano-TiO₂ particles as the products of hydration of the cement paste are deposited at the surface of these particles and continue to grow, forming conglomerates containing nanoparticles as the core. This means that the nano-TiO₂ particles, dispersed in the cement matrix, contribute to density, and improve the mechanical characteristics of cement composites.

It should be noted that the nano-TiO₂ modifiers fill pores in the structure of the mortar, which is shown on a microphotograph. The samples from TiO₂ P25 (Fig. 4, *a*) and TiO₂/S, C (Fig. 4, *b*) create a compacted surface with pores in the range of 0.1–1.0 μm. This distribution of pores ensures the effectiveness of photocatalysis reactions as it increases the specific area of the surface. This indicates that nano-TiO₂ is capable of filling pores in the cement matrix, reducing the size of C-S-H crystals, and sealing the microstructure of cementing composites.

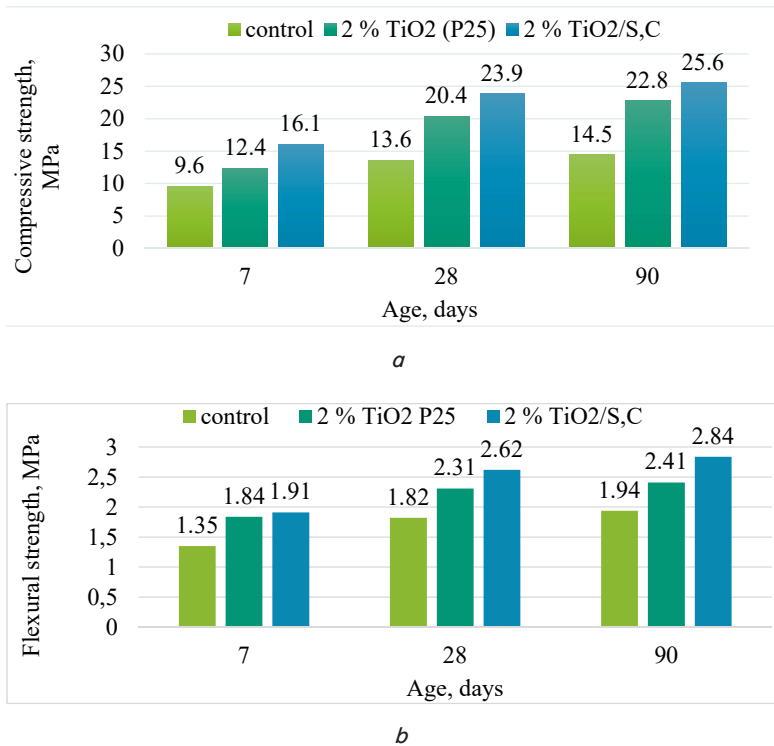


Fig. 2. Strength of the nanomodified photocatalytic cement mortars: *a* – compressive; *b* – flexural

An important characteristic of the additive for cement mortars is the ratio of reflection of light by surface. The nano-modifier TiO₂ P25 has the highest value of this coefficient, compared to other common components of mortars (Fig. 3).

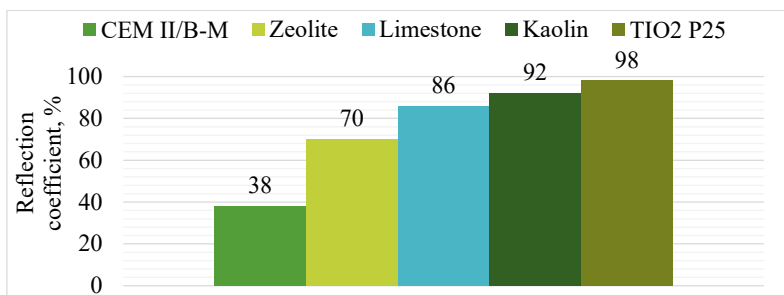
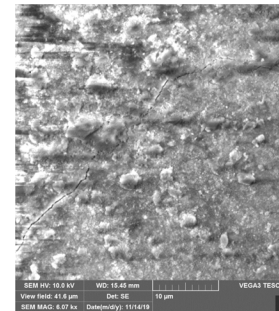
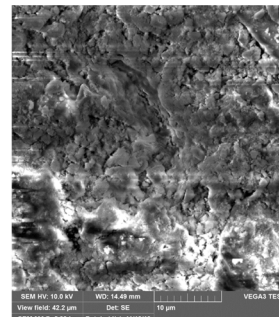


Fig. 3. Cement mortar reflection coefficient

An analysis of the X-ray phase analysis data on the modified cement mortars indicates that in the presence of high enough intensity lines of β-SiO₂ ($d/n=0.425$; 0.334 nm) the cement stone demonstrates the calcite lines ($d/n=0.302$; 0.228 nm) and calcium hydroxide ($d/n=0.492$; 0.263 nm). In addition, the stone with an additive of TiO₂/S,C shows minor lines of ettringite ($d/n=0.973$; 0.561 nm).



a



b

Fig. 4. SEM-images of cement mortars samples: *a* – 2.0 wt. % of TiO₂ P25; *b* – 2.0 wt. % of TiO₂/S,C

Fig. 5 shows the morphology of TiO₂ nanoparticles, doped with sulfur (S) and carbon (C). Hence it is evident that the nano-composite TiO₂/S, C has a much larger specific surface area than the available analog of pure nano-sized TiO₂ P25, and, therefore, the increased photocatalytic activity. According to [27], the surface layers of the TiO₂/S, C powder nanoparticles contain 10 times more sulfur ions compared to the volumetric content, indicating the segregation of S⁶⁺ to the surface of the anatase nanoparticles.

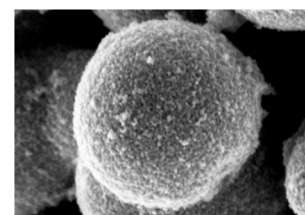


Fig. 5. SEM –image of the agglomeration of TiO₂/S, C crystals

5. 2. Studying the photocatalytic activity of the modified cement mortars

When determining the photocatalytic activity of samples, we acquired the radiation indicators of rhodamine before irradiation, and 1 and 2 hours after irradiation (Fig. 6). The results in Fig. 6, *a* shows that a sample containing 2.0 wt. % of TiO₂/S, C has the highest level of photocatalytic activity (87 %) in the visible spectrum of light. It should be noted that the photocatalytic activity of the surface of samples containing the TiO₂ P25 and TiO₂/S, C nanopowders differ significantly due to the properties of the TiO₂/S, C nanocomposite to operate in the visible spectrum of light. Fig. 6, *b-d* shows the photographs of rhodamine discoloration before irradiation, after 1 hour of irradiation, and after 2 hours of irradiation, at the surface modified by 2.0 wt. % of TiO₂/S, C.

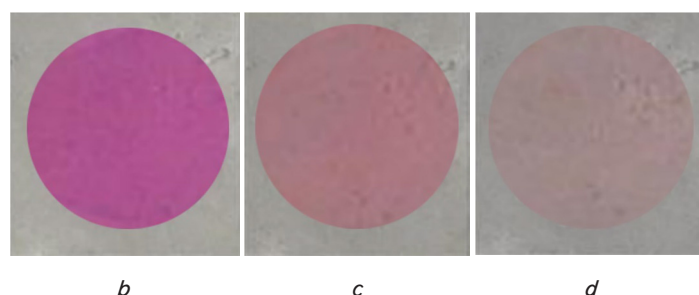
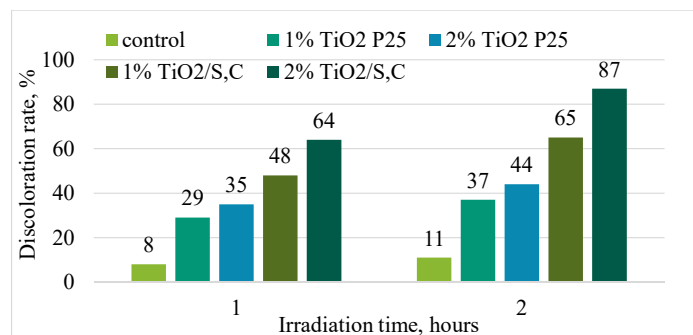


Fig. 6. Photocatalytic degradation of the colorant Rhodamine B: *a* – diagram of the degree of discoloration; *b* – a drop of the colorant before irradiation; *c* – a drop of the colorant after 1 hour of irradiation by a laser; *d* – a drop of the colorant after 2 h of laser irradiation

5. 3. Studying the hydrophobic properties of the surfaces of cement mortars when using the nanomodifiers TiO₂ P25 and TiO₂/S, C

When determining the hydrophobic properties of the samples' surfaces, the measurement was carried out using an optical method (Fig. 7, *a-c*) to determine the angle of contact between the water and mortar surface (Fig. 7, *d*). The contact angle of the control sample surface is only 38.4° (Fig. 7, *a*), while the non-modified TiO₂ P25 provides the surface with the hydrophobic properties, creating a contact angle of 108.6° (Fig. 7, *b*). According to Fig. 7, *c*, the sample modified with 2.0 wt. % of TiO₂/S, C has the largest contact angle with a droplet (120.8°). Based on these results, it can be stated that the nanopowders TiO₂/S, C and TiO₂ P25 provide the surface of the cement mortar with the hydrophobic properties.

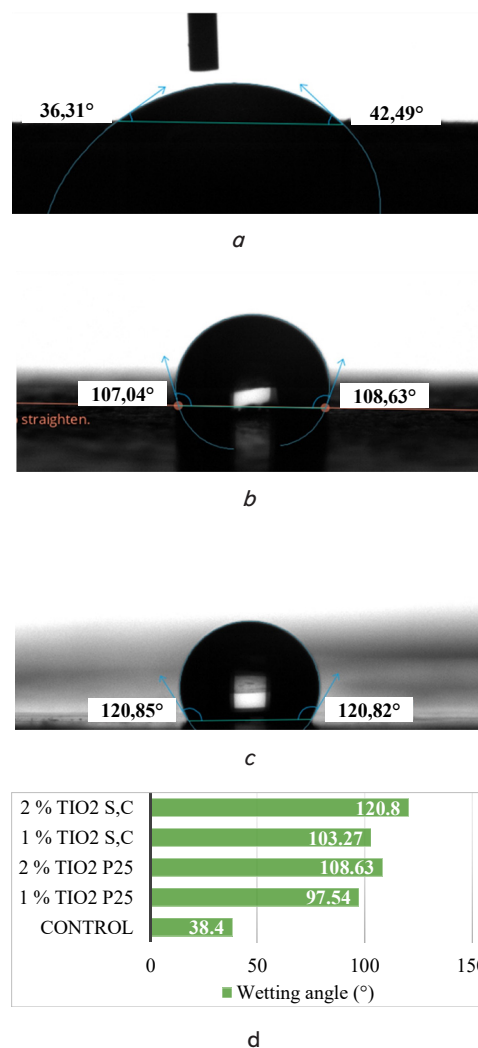


Fig. 7. Determining the contact angle of wetting with water: *a* – angle of contact with the surface of the control mortar; *b* – angle of contact with the surface of the mortar, modified with 2.0 wt. % of TiO₂ P25; *c* – angle of contact with the surface of the mortar, modified with 2.0 wt. % of TiO₂/S, C; *d* – histogram of the angle of wetting with the surface

5. 4. Determining the indicators of free energy for the surfaces of the modified compositions of cement mortars

In order to determine the indicators of free surface energy, we determined the contact angle of the -Bromophthalene liquid with the surfaces of the control and modified compositions (Fig. 8). Our results showed that the largest angle of contact is achieved at the surface of the sample modified with 2.0 wt. % of TiO₂/S, C (112.6°), while the angle of contact of the control sample was 30.4°. The findings confirm experimental studies of determining the contact angle with water and prove that titanium dioxide, doped with sulfur and carbon, has the best hydrophobic properties for cement mortars.

When determining the free surface energy using an OWRK method (Fig. 9), it was found that the modifiers TiO₂ P25 and TiO₂/S, C reduce the indicators of free surface energy. The lowest indicator of the free surface en-

ergy was registered for the cement mortar modified with 2.0 wt. % of TiO₂/S, C (40.1 mJ/m²). The highest value of the free surface energy (64.1 mJ/m²) characterizes the control sample. These results indicate that the modification of cement mortars with nano-TiO₂ renders them the hydrophobic properties.

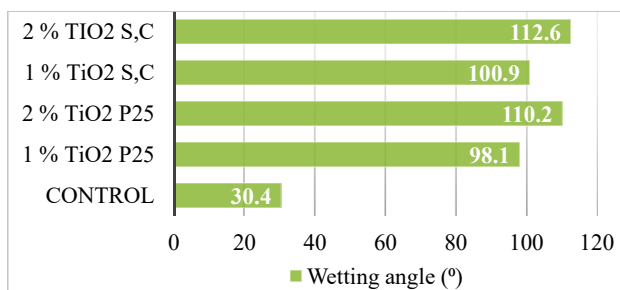


Fig. 8. Histogram of the wetting angle of α-Bromophthalene

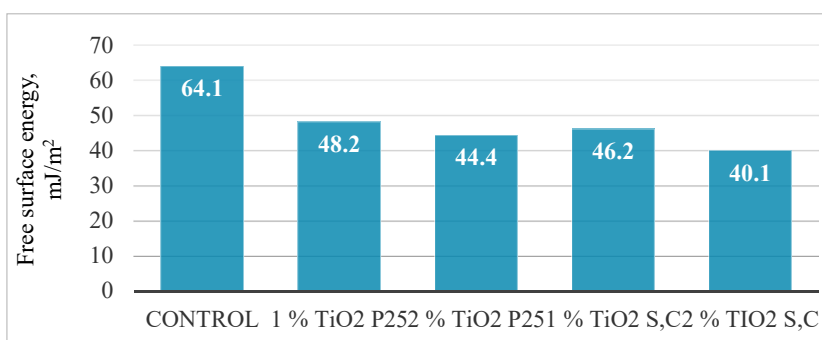


Fig. 9. Values of the free surface energy (mJ/m²) of cement mortar samples based on an OWRK method

Thus, the TiO₂/S, C nanocomposite exerts a comprehensive effect on cement mortars. Experimental studies confirmed that between 1.0 wt. % and 2.0 wt. % of TiO₂/S, C, the best indicators of the photocatalytic, physical-mechanical, and hydrophobic properties are achieved when adding 2.0 wt. % of TiO₂/S, C. The study results suggest that the application of the TiO₂/S, C nanocomposite makes it possible to create advanced finishing surfaces that can promote the self-cleaning processes in the visible spectrum of light. In this regard, the photocatalysis of cement materials is the best choice for reducing the costs associated with the repair and maintenance of facades in a building.

6. Discussion of results of studying the properties of the nanomodified photocatalytic cement mortars with hydrophobic properties

According to the results of our study into the influence of the nanomodifiers TiO₂ P25 and TiO₂/S, C on the particle size distribution in the cementing systems, it was found that during the initial period of the structure formation the surface area with 2.0 wt. % of TiO₂ P25 is an order of magnitude larger than that in the entire system (Fig. 1). This indicates that the ultra size fraction of titanium dioxide is the main factor in increasing of the surface area of the cement mortar.

When determining the nanomodification effectiveness of cement-sand mortars using the TiO₂ P25 and TiO₂/S, C additives in conjunction with ethers of polycarboxylate, as evidenced by the results obtained (Fig. 2), we have shown the possibility of increasing the strength of cement mortar.

Thus, the strength of the sample with 2.0 wt. % of TiO₂/S, C grows by 75 % compared to control composition. This is achieved both by decreasing the water cement ratio and dispersing the nanopowder of titanium dioxide in the mortar.

It is demonstrated that the introduction of TiO₂ P25 and TiO₂/S, C predetermines the compaction of the microstructure of a cement composite as nano-TiO₂ is capable of filling pores in the cement matrix, reducing the size of portlandite crystals. It should be noted that the surface of the modified samples is covered with pores measuring 0.1–1.0 μm, which makes it possible to improve the mechanical properties of cement mortars (Fig. 4).

Of particular interest is to compare the influence of nano-TiO₂ and the TiO₂/S, C nanocomposite on the photocatalytic surface efficiency. It has been found that titanium dioxide (TiO₂/S, C), doped with sulfur, shows a significantly higher photocatalytic activity than the samples contain-

ing TiO₂ P25. The sample with 2.0 wt. % of TiO₂/S, C demonstrated the highest indicators (87 %) in the degradation of the colorant from the surface, which is 2 times larger compared to that with 2.0 wt. % of TiO₂ P25 (Fig. 6). It should also be noted that samples from the TiO₂/S, C nanocomposite are able to initiate photocatalysis reactions in the visible spectrum of light, generating free radicals and thereby neutralizing pollutants on the surface without additional UV irradiation. It follows then that the introduction of TiO₂/S, C nanoparticles with the photocatalytic properties in the visible range of light to the construction sector opens up wide possibilities for the manufacture of self-disinfecting surfaces.

A significant factor in the study of the influence of the modifiers TiO₂ P25 and TiO₂/S, C is also that the surfaces acquire hydrophobic properties. According to the results of study, TiO₂/S, C provides the surface with hydrophobic characteristics, increasing the angle of contact between water and the surface (Fig. 7). Hydrophobicity increases the operational life of the surface and retains its aesthetic characteristics. Results on determining the free energy of the surfaces (Fig. 8, 9) confirmed the hydrophobic properties of the modifiers TiO₂ P25 and TiO₂/S, C.

Thus, according to the results from a series of experiments, it can be considered that the TiO₂/S, C nanocomposite has a comprehensive effect on cement mortars. However, the issue of uniform dispersion of the conglomerations of titanium dioxide nanoparticles in the structure of the mortar remains insufficiently studied. Another important issue is the ability of TiO₂/S, C to neutralize nitrogen oxides (NO_x) in the air, which is achieved through the photocatalytic properties of surfaces. At the same time, to fully evaluate the effectiveness of the TiO₂/S, C nanocomposite, it is necessary to conduct research into the interaction with other types of nanomodifiers to create multifunctional building materials, which defines the further direction for the current study. The impact of nano-TiO₂ on cement mortars may vary depending on the type of the cement matrix, water/cement ratio, the nano-TiO₂ content, its type, as well as the extent of dispersion. Therefore, identifying the impact of adding photocatalysts based on different modifications of nano-TiO₂ on the microstructure of a cement composition

and the durability of finishing mortars is an important active area of further research.

7. Conclusions

1. The studies have shown the influence of the nano-TiO₂ modifiers on the physical and mechanical, photocatalytic, and hydrophobic properties of cement mortars. Given the results obtained, it can be proved that the dioxide of titanium, doped with sulfur and carbon, in conjunction with the addition of ether of polycarboxylate increases the strength of cement mortar by 75 % compared to control sample due to the extremely high surface activity.

2. Special features in the formation of the photocatalytic properties of the cement mortar, containing nano-sized titanium dioxide, are determined largely by the macropores at the surface of the samples. Due to this mechanism, when applying ultrasonic dispersion, the area of the surface of the cement mortar increases, which contributes to the increase in photocatalytic activity. The colorimetric study has deter-

mined the effectiveness of mortars with the addition of titanium dioxide at the degradation of the colorant of rhodamine B from the samples' surfaces. When adding 2.0 wt. % of TiO₂/S, C the surface is cleaned by 87 % after 2 hours of irradiation by a low-intensity laser with a wavelength of 532 nm.

3. Our study has found the effect of the nano-TiO₂ additives on the hydrophobic properties of cement mortar surfaces. It is established that the surface acquires hydrophobic characteristics when adding 2.0 wt. % of TiO₂/S, C while the angle of contact is 120.8°. When determining the indicators of free energy of the surface, it is established that with an increase in the amount of titanium dioxide in the volume of the mortar, the energy of the surface decreases, which indicates the improvement of the operational characteristics of such mortars.

4. It has been determined that the improved characteristics are achieved when adding 2.0 wt. % of TiO₂/S, C. When analyzing the results from determining the free surface energy, it was found that the TiO₂ P25 and TiO₂/S, C modifiers reduce the indicators of free surface energy. The lowest indicator of the free surface energy was registered for the cement mortar modified with 2.0 wt. % of TiO₂/S, C (40.1 mJ/m²).

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