Original papers
Advanced structural materials, materials for extreme conditions

УДК 620 DOI: 10.17277/jamt-2025-10-01-032-039

The effect of silica-modified carbon nanotubes additive to alkyd enamel coating on adhesion, corrosion resistance and bonding of reinforcement with cement

© Mustafa T. A. Al-Khalidi[a]✉, Alexander N. Blokhin [a]

[a] *Tambov State Technical University, Bld. 2, 106/5, Sovetskaya St., Tambov, 392000, Russian Federation*

✉ mustafa_alkhalidi@mail.ru

Abstract: In this paper, the effect of carbon nanotubes coated with silicon dioxide, used as a filler in alkyd enamel PF-115, on the adhesion strength of the modified alkyd enamel paint to steel reinforcement and on the adhesion of reinforcement coated with modified alkyd paint to concrete was investigated. The adhesive tape method (ASTM D3359 Standard) was used to study the adhesion strength. To test the effect of the corrosion resistance of the coating on the adhesion strength between the coated reinforcement and concrete, the samples were subjected to a preliminary accelerated corrosion process in a sodium chloride solution under the influence of a direct electric current of 0.5 A, after which pull-out tests were carried out. The results showed that with an increase in the nanofiller content, the adhesion strength decreases insignificantly, and the force for pulling out reinforcement from concrete increases for the coated samples with an increase in the nanofiller concentration to 0.349 wt. %, after which it begins to decrease. The improvement in the overall corrosion resistance characteristics of the coating after the application of a modified alkyd enamel used as a protective coating for steel reinforcement containing carbon nanotubes with silica with a concentration of 0.349 wt. % was established.

Keywords: coating adhesion; anticorrosive coatings; nanocoating; nanotechnology; tensile test.

For citation: Al-Khalidi MTA, Blokhin AN. The effect of silica-modified carbon nanotubes additive to alkyd enamel coating on adhesion, corrosion resistance and bonding of reinforcement with cement. *Journal of Advanced Materials and Technologies*. 2025;10(1):032-039. DOI: 10.17277/jamt-2025-10-01-032-039

Влияние добавки модифицированных диоксидом кремния углеродных нанотрубок в алкидное эмалевое покрытие на адгезию, коррозионную стойкость и связь арматуры с цементом

© М. Т. А. Аль-Халиди [a]✉, А. Н. Блохин [a]

[a] *Тамбовский государственный технический университет,*
ул. Советская, 106/5, пом. 2, Тамбов, 392000, Российская Федерация

✉ mustafa_alkhalidi@mail.ru

Аннотация: В настоящей работе исследовано влияние углеродных нанотрубок, покрытых диоксидом кремния, используемых в качестве наполнителя алкидной эмали ПФ-115, как на прочность сцепления модифицированной алкидной эмалевой краски со стальной арматурой, так и на сцепление арматуры, покрытой модифицированной алкидной краской, с бетоном. Для исследования прочности сцепления использовался метод клейкой ленты (стандарт ASTM D3359). Для проверки влияния коррозионной стойкости покрытия на прочность сцепления между покрытой арматурой и бетоном образцы подвергли предварительному ускоренному процессу коррозии в растворе хлорида натрия при воздействии постоянного электрического тока силой 0,5 А, после чего провели испытания на выдергивание. Результаты показали, что по мере увеличения содержания нанонаполнителя прочность адгезии снижается незначительно, и сила для выдергивания арматуры из бетона увеличивается для покрытых образцов с увеличением концентрации нанонаполнителя до 0,349 мас. %, после чего начинает уменьшаться. Установлено улучшение общих характеристик коррозионной стойкости покрытия после применения модифицированной алкидной эмали, используемой в качестве защитного покрытия стальной арматуры, содержащей углеродные нанотрубки с кремнеземом с концентрацией 0,349 мас. %.

Ключевые слова: адгезия покрытий; антикоррозионные покрытия; нанопокрытия; нанотехнологии; испытание на растяжение.

Для цитирования: Al-Khalidi MTA, Blokhin AN. The effect of silica-modified carbon nanotubes additive to alkyd enamel coating on adhesion, corrosion resistance and bonding of reinforcement with cement. *Journal of Advanced Materials and Technologies*. 2025;10(1):032-039. DOI: 10.17277/jamt-2025-10-01-032-039

1. Introduction

Corrosion is a common problem in the construction industry as it leads to the destruction of structures as well as costly repairs [1, 2].

Corrosion protection in construction plays a key role in ensuring the durability and safety of the structures being erected. Corrosion of metal structures such as beams, frames and reinforcement can lead to serious consequences, including reduced strength, deformation and even collapse of buildings and bridges. This not only threatens human lives but also entails significant economic losses.

Various methods are used to prevent corrosion in construction. One of them is the use of high-quality corrosion-resistant materials in the construction of structures. Also widely practiced is the application of protective coatings, such as paints and varnishes containing anti-corrosion components that create a barrier between the metal and the aggressive environment.

As a result, the use of integrated approaches to corrosion protection contributes to a significant increase in the service life of construction projects and maintains their reliability at a high level.

In reinforced concrete structures made with steel reinforcement, corrosion often occurs due to contact of water or air with the reinforcement. Various methods are used to combat it [3–8], including the application of anti-corrosion paint. Thus, it serves as a barrier to the penetration of corrosion factors onto the metal surface.

Recently, there has been an increase in attention to anti-corrosion nanocoatings. This type of coating is based on nanomaterials that have certain characteristics that increase their effectiveness [9, 10].

In [11], the effect of silica-coated graphene oxide nanosheets with 0.1 % epoxy coating on the mechanical properties and corrosion resistance was investigated. The results showed that the adhesion strength of epoxy coatings on steel substrates was significantly improved by the addition of nanofillers. The corrosion resistance test results also showed that the corrosion protection performance of epoxy coatings was significantly enhanced by the incorporation of nanofillers, provided that they were well distributed in the coating matrix.

In another study [12], a new anticorrosive nanocomposite coating was developed based on nano-CoS_2 modified epoxy resin. The anticorrosive properties of the coating were studied using electrochemical impedance spectroscopy (EIS) as well as tensile tests to measure the adhesion strength. The results showed that the anticorrosive properties of the modified coating were significantly improved compared to the neat epoxy coating. In addition, the tensile test results showed that the adhesion of the coating was significantly improved after the addition of nanofillers.

It is worth noting that, to our knowledge, no studies have been conducted on the effect of the concentration of added nanofillers in the polymer coating on the adhesion strength of reinforcing steel to concrete.

This study is devoted to the study of the effect of modifying alkyd enamel coatings with carbon nanotubes with silica on the adhesion and bonding to cement for reinforced bars. The aim of the study is to develop improved and durable anti-corrosion coatings for reinforced concrete structures.

2. Materials and Methods

2.1. Materials

In the present study, commercial alkyd enamel PF-115 (Faktor LLC, Russia) was chosen as a matrix for obtaining modified nanocomposite coatings, taking into account its wide application and production range, as well as its anticorrosive properties [13]. Multi-walled carbon nanotubes (MWCNTs) of the “Taunit-M” series (NanoTechCenter LLC, Tambov, Russia) modified with a thin layer of silicon oxide were used as a nanofiller. To improve the dispersion of nanotubes in the polymer matrix, a non-ionic surface-active agent Triton X-100 (PanEco LLC, Russia) was used. Tetraethyl orthosilicate purchased from the company “Reaktiv Express” (Moscow, Russia) served as a precursor for obtaining silicon oxide. Commercial white spirit (Leroy Merlin, Russia) was used as a solvent. The resulting composite coating was applied by airbrushing (Nasedal, China) onto substrates made of 8 mm diameter corrugated steel and AISI 303 sheet steel.

2.2. Modification of carbon nanotubes with silicon oxide

Modifying carbon nanotubes (CNTs) with silicon oxide (SiO_2) is an effective method to improve their properties and expand their applications. This process, known as encapsulation, creates a core-shell structure of CNT@SiO_2 that combines the unique characteristics of both materials.

The main advantage of encapsulating CNTs with silica is the improvement of electrical insulation and suppression of the high electrical conductivity of carbon nanotubes. This makes them more suitable for use in specific areas where a combination of mechanical strength and electrical insulation is required [14, 15].

Encapsulated CNTs also exhibit increased thermal stability and improved interfacial interaction with polymer matrices. This interaction facilitates the creation of polymer nanocomposites with high mechanical strength.

The process of obtaining CNT@SiO_2 involves treating carbon nanotubes with a solution of tetraethyl orthosilicate (TEOSi) in the presence of a catalyst such as ammonia (NH_4OH). As a result, Si–O–C bonds are formed, which ensure strong binding of SiO_2 to the surface of CNTs.

Thus, modification of carbon nanotubes with silicon oxide opens up new possibilities for their use in building materials that require a combination of mechanical strength, electrical insulation and thermal stability.

2.3. Preparation of modified coating

The nanomodified coating was synthesized in two stages. In the first stage, the initial nanotubes were oxidized in concentrated nitric acid to create oxygen-containing functional groups on the surface. The resulting oxidized CNTs (50 g) were dispersed in a mixed solvent of ethanol-ammonia (35 : 1).

Tetraethoxysilane (TEOS) (6.25 ml) was added to the resulting suspension, initiating the process of hydrolysis and condensation with the formation of silicon dioxide particles on the surface of the nanotubes. After 9 hours of stirring at room temperature, the product was thoroughly washed and dried.

In the second stage, the obtained CNTs coated with silicon dioxide were dispersed in a mixture of white spirit and alkyd enamel paint (ratio 1 : 9) using a stirrer and applied with an airbrush onto pre-prepared metal substrates. To obtain different concentrations of nanofillers, the modified paint was mixed with paint diluted with white spirit and unmodified paint (the dilution ratio was also 1 : 9). Table 1 below shows the mass concentration of nanofillers relative to the dried coating layer.

Table 1. Concentrations of nanofiller in coating layers of different samples

Sample No	Weight of substrate without coating, g	Substrate weight after first coating, g	Weight of nanofiller in the first wet layer of coating, g	Substrate weight one hour after the first coat has dried, g	Substrate weight after the second layer of coating, g	Weight of nanofiller in the second wet coating layer, g	Weight of the substrate after drying of the second layer of coating, g	Percentage of nanofillers in dry coating, wt. %
1	153.52	154.34	0	154.29	155.12	0	155.01	0
2	159.1	159.94	0.00033	159.88	160.67	0.000316	160.57	0.044
3	160.42	161.21	0.00063	161.16	161.97	0.000648	161.86	0.089
4	154.54	155.4	0.00103	155.35	156.13	0.000936	156.05	0.13
5	160.4	161.21	0.00129	161.14	161.97	0.001328	161.89	0.176
6	159.71	160.56	0.0017	160.51	161.25	0.00148	161.16	0.219
7	160.4	161.19	0.00189	161.13	161.94	0.001944	161.87	0.261
8	160.4	161.28	0.00246	161.23	162.09	0.002408	161.99	0.31
9	161.74	162.65	0.00291	162.59	163.21	0.001984	163.14	0.349
10	159.92	160.68	0.00273	160.63	161.47	0.003024	161.4	0.389
11	158.94	159.83	0.00356	159.77	160.51	0.00296	160.44	0.435

Table 2. Data on the concrete mixture used to prepare the samples (kg of material per cubic meter of concrete)

Material	Material weight, kg
Cement (Modifier 300, Turkey)	475
Water	210
Coarse aggregate(520 mm)	790
Fine aggregate (1–3 mm)	552
Quartz sand (0.1–0.4 mm)	372
Super plasticizer (BETONAC 135, Turkey)	0,9

2.4.Preparation of cement mixture

In order to prepare the samples required for testing the adhesion of reinforcing steel to concrete, the concrete mixture was prepared in the proportions given in Table 2.

2.5. Coating adhesion test

Coating adhesion test is one of the methods for measuring the bond strength between a coating and a surface. To perform this test, a sample was first prepared and the coatings were applied to metal substrates using an airbrush so that the average coating layer thickness after drying was at least 80 microns.

After this, a notch was made on the sample surface (in the form of a network of perpendicular lines) using a knife, the distance between each notch was about 2 mm. Then, after cleaning the notch, adhesive tape was glued to the cut, which was removed by pulling it in a direction perpendicular to the surface of the sample.

The peeling process takes a few seconds. Adhesion is assessed by analyzing the coating condition after removing the test strip. ASTM D5539 Method B should be used as a guide for evaluation.

2.6. Cement reinforcement pull-out test

This test is carried out by measuring the force required to pull out reinforcement coated with anti-corrosion paint after exposing the specimens to corrosive factors and comparing the measured values with the force required to pull out uncoated reinforcement from concrete (control specimen).

The specimen was reinforced with one steel bar 500 mm long and 14 mm in diameter, located in the centre of the specimen. The dimensions of the specimen are shown in Fig. 1 below.

Eleven specimens were prepared and subjected to an accelerated corrosion process for 10 days using a DC power source.

The specimens were placed in a 3.5 wt. % NaCl solution in a container, the NaCl solution was added to the container to a height of 20 cm from the bottom of the sample. Each specimen was connected to the positive electrode of the power source and was used as an anode. The cathode was a rectangular steel plate of 300 × 350 mm, immersed in the tank and connected to the negative terminal of the power source shown in Fig. 2.

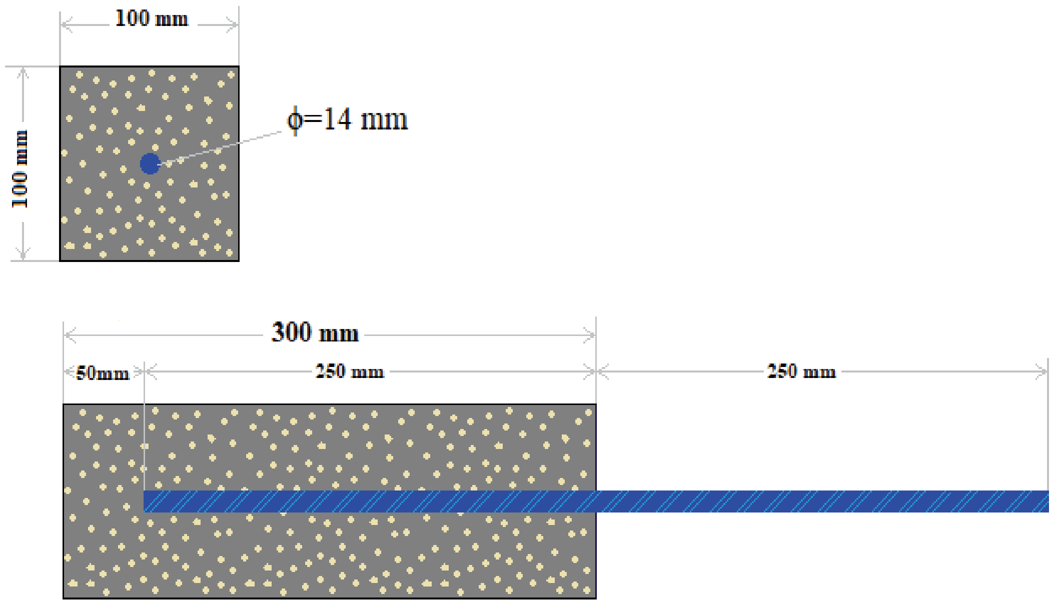

Fig. 1. Preparation of specimens for testing adhesion of cement reinforcement

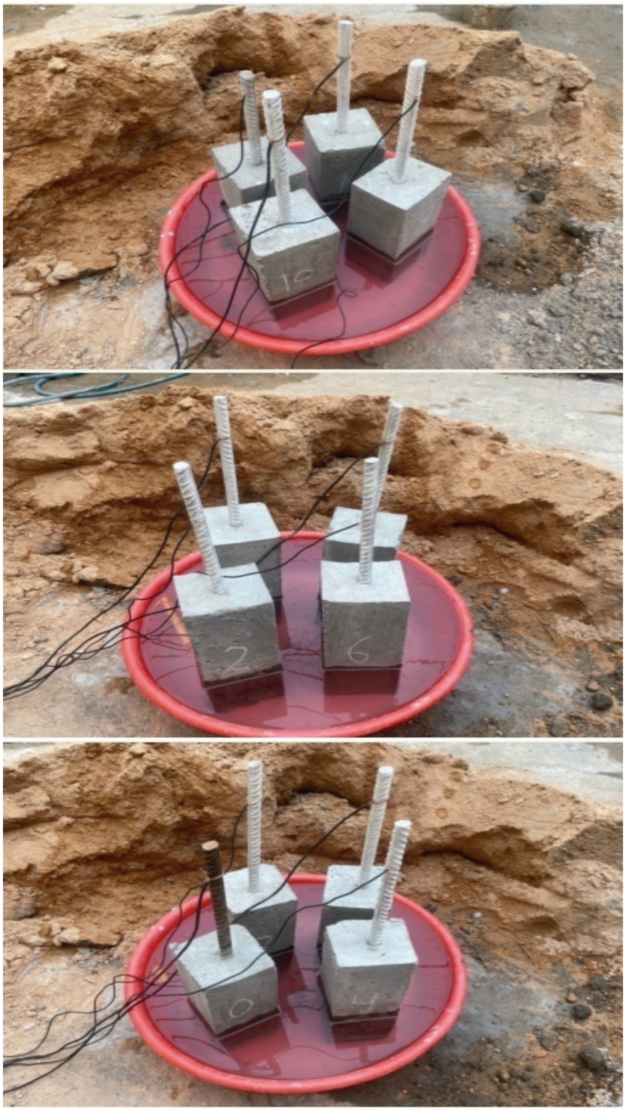

Fig. 2. Specimens in a test tank

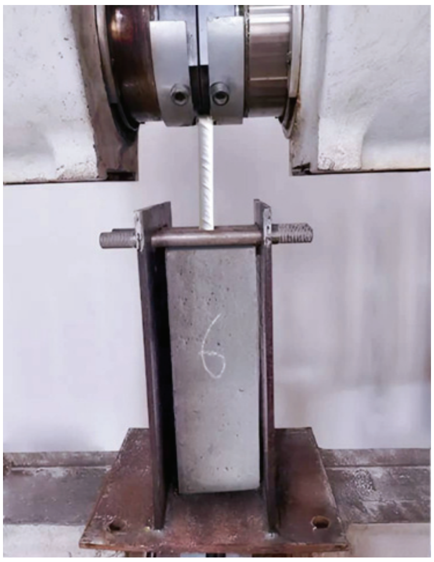

Fig. 3. Pull-out test setup

The reinforcement in the specimens was connected to the power source in parallel and subjected to a constant electric current of 0.5 A. The electric current was adjusted so that it remained constant during the corrosion process.

After completion of the accelerated corrosion, a pull-out test was conducted on a universal testing machine to test the effect of the nanomaterial coating on the bond strength of the corroded reinforcing steel.

The applied load was controlled by a computer using displacement control. The tensile and sliding load between the steel bar and concrete was measured by a universal testing machine. Figure 3 below shows the pull-out test.

3. Results and Discussion

3.1. Coating adhesion test

The results of the coating adhesion test showed that the coating adhesion was very good up to the 9th specimen, as there were few delaminations on the tape. The adhesion decreased with the increase of the nanofiller percentage, but the adhesion maintained normal values up to the 11th coating specimen. Table 3 below shows the adhesion values for the coatings with metal substrates.

These results can be explained by the fact that at low concentrations of nanofillers, the effect of the filler on the shape of the polymer matrix and on the surface area of contact of the polymer molecules with the substrate was minimal, so it had little effect on the adhesion of the coating.

Table 3. Values of coating adhesion indicators to metal substrates

Specimen No	Adhesion index
1	B4
2	B4
3	B4
4	B4
5	B4
6	B4
7	B4
8	B4
9	B4
10	B3
11	B3

However, as the percentage of nanofillers increased, the area occupied by nanoparticles on the surface of contact of the coating with the metal substrate increased due to a decrease in the surface area of contact of the polymer molecules with the substrate, which weakened the adhesion.

In addition, cracks that occur in the paint layer as a result of tensile stresses during its drying, in turn, are a consequence of large distortions of the structure of the polymer matrix as a result of the agglomeration of carbon nanotubes coated with silicon dioxide, which led to a decrease in the contact area of the polymer molecules with the metal substrate and caused a further decrease in the adhesion strength.

Despite the decrease in adhesion strength due to the agglomeration of carbon nanotubes in specimens 10 and 11, the paint retained good adhesion to the substrate due to the strong adhesion provided by the alkyd enamel.

3.2. Cement reinforcement pull-out test

Initially, the load-slip curves showed a linear behavior at the initial stage of loading in all specimens, and then showed a nonlinear response. Corrosion had a significant effect on the adhesion and slip behavior of reinforced concrete specimens. With the increase of the percentage of nanofillers in the coating layer to 0.349 wt. %, the change in the final bearing capacity decreased by 17.3 %, and the change in slip increased to 69.4 % (all measurement values are shown in Table 4).

Table 4. Pull-out test results

Specimen, wt. %	Maximum load, kN	Maximum sliding, mm
Without coating	51.8	3.6
0	33.3	2.4
0.044	34.6	2.2
0.089	36.5	2.1
0.130	38.0	2.0
0.176	39.0	1.9
0.219	38.8	1.5
0.261	40.2	1.3
0.310	41.1	1.2
0.349	42.8	1.1
0.389	40.9	1.3
0.435	32.0	2.6

Figure 4 below shows the load-slip curve for all the specimens studied.

After the above-mentioned concentration of nanomaterials, the change in the final bearing capacity slightly increased and then increased significantly, while the change in slip first decreased slightly and then decreased significantly. These results can be interpreted as follows: The decrease in the magnitude of the change in the ultimate load, with an increase in the concentration of nanofillers in the coating layer to 0.349 wt. %, the corrosion resistance of the coating increases.

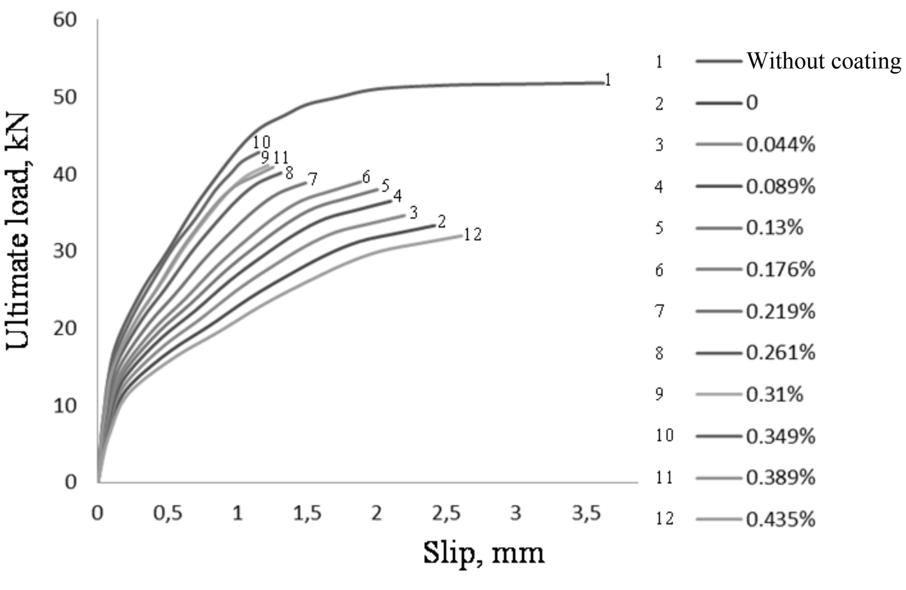

Fig. 4. Load-slip curve for all samples studied

As the density of the coating layer increases (barrier effect), its electrical resistance also increases, which significantly reduces the formation of iron corrosion products (rust), which, on the one hand, has a much weaker bond with concrete than reinforcing steel, and on the other hand, causes cracks in the concrete matrix as a result of increased pressure. Since the volume of corrosion products is greater than the volume of the original steel, this leads to a decrease in the contact surface area between the reinforcement and concrete.

It should be noted that good adhesion of the coating to the reinforcement in specimens up to a nanofiller concentration of 0.349 wt. % by weight plays an important role in increasing the force required to pull the reinforcement out of concrete. Since improved adhesion prevents the penetration of corrosive agents under the coating to the reinforcement, which limits the occurrence and spread of corrosion over the metal surface, which in turn maintains high adhesion strength of the reinforcement to the concrete matrix.

However, after the specified limitation of the percentage of nanofillers, agglomeration of nanoparticles begins to appear, causing a weakening of the adhesion of the coating layer to the reinforcement steel, which allows corrosive agents to reach the metal surface and cause corrosion.

As for the sliding of reinforcement in concrete during pull-out tests, with an increase in the percentage of nanofillers in the coating layer to 0.349 wt. %, the sliding before the metal exits the concrete sample decreases. This is the result of the synergy of two factors: first, an increase in roughness with CNTs, which leads to an increase in adhesion between the coating, reinforcement and concrete and the friction coefficient. The second factor is an increase in the strength of the coating itself. The combined effect of these two factors allows the reinforcement to maintain sufficient friction force so that the remaining part of it inside the specimen is sufficient to prevent the reinforcement from being completely pulled out of the specimen.

The decrease in the change in slip that occurs before the reinforcing steel leaves the specimen after the above limit of the concentration of nanofillers in the coating occurs as a result of a decrease in the friction force between the coated reinforcing steel and the concrete as a result of increased formation of corrosion products, which adhere weaker to the concrete.

4. Conclusion

The test results showed an improvement in the overall corrosion resistance characteristics of the coating after the modification proposed in the article. The study of nanomodified coatings showed that the adhesion degree increased up to the 9th specimen. A decrease in adhesion was observed with an increase in the percentage of nanofillers, but the adhesion remained high up to the 11th coating specimen. The pulling force for pulling out reinforcing steel from concrete increased for the coated samples with an increase in the nanofiller concentration to 0.349 wt. %, after which its value began to decrease. The recommended percentage of additives of carbon nanotubes coated with silicon oxide to improve the corrosion performance of the coating is 0.349 wt. %.

5. Funding

This study received no external funding.

6. Conflict of interest

The authors declare no conflicts of interest.

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Information about the authors / Информация об авторах

Mustafa T. A. Al-Khalidi, Postgraduate Student, Tambov State Technical University (TSTU), Tambov, Russian Federation; ORCID 0009-0008-2391-4995; e-mail: mustafa_alkhalidi@mail.ru

Alexander N. Blokhin, Cand. Sc. (Eng.), Associate Professor, TSTU, Tambov, Russian Federation; ORCID 0000-0002-5875-5962; e-mail: cha-cha@rambler.ru

Аль-Халиди Мустафа Тамер Али, аспирант, Тамбовский государственный технический университет (ТГТУ), Тамбов, Российская Федерация; ORCID 0009-0008-2391-4995; e-mail: mustafa_alkhalidi@mail.ru

Блохин Александр Николаевич, кандидат технических наук, доцент, ТГТУ, Тамбов, Российская Федерация; ORCID 0000-0002-5875-5962; e-mail: cha-cha@rambler.ru

Received 21 January 2025; Revised 19 February 2025; Accepted 24 February 2025