Detonation Nanodiamonds as Part of Smart Composite Paintwork Materials

Gurina Galina[1][0000-0002-7547-5508], Kozub Pavlo[2][0000-0002-7162-027X], Kozub Svetlana[3][0000-0002-3049-1555], Saienko Natalia [4][0000-0003-4873-5316] and Skripinets Anna [4][0000-0002-2340-023X]

[1] Kharkiv National University of Urban Economics named after O.M. Beketov, 61002,
Kharkiv, Ukraine
[2] Kharkiv National University of Radio Electronics, 61166, Kharkiv, Ukraine
[3] Kharkov National Medical University, 61000, Kharkiv, Ukraine
[4] Kharkiv National University of Civil Engineering and Architecture, 61002,
Kharkiv, Ukraine
saienko.nataliia@kstuca.kharkov.ua

Abstract. The development of materials using fillers of polymer matrices with micron and submicron levels of dispersion has largely exhausted itself in achieving a new level of performance. New breakthrough solutions can be reached using the principles of nanotechnology, using the nano dispersed state of reinforcing components, the synthesis of which is very promising both theoretically and practically from the point of view of creating smart composite paints and varnishes. Such nano dispersed particles are nanodiamonds - promising representatives of carbon nanostructures, which have a crystal lattice characteristic of ordinary diamond: planaxial class of cubic syngony, two face-centered Brave lattices, shifted relative to each other by 1/4 of the main diagonal from each diagonal, but 10 nm. The aim of the work was to study the effect of nanodiamond particle additives on the physical-mechanical and optical properties of nanocomposite paints and prediction of their further use in various industries. It is established that the introduction of nanodiamonds leads to the increased wear resistance of paints and varnishes and leads to a decrease in ultraviolet radiation under the coating. According to research, detonation nanodiamonds are recommended for the production of water-based nanocomposite acrylic polymers in various industries to create coatings to absorb ultraviolet radiation and improve their physical and mechanical properties.

Keywords: Nanodiamonds, Paint Coatings, Wear Resistance, Ultraviolet Radiation.

1 Introduction

A promising way to solve the problems of development of chemistry and chemical technologies of in Ukraine is the creation of innovative materials based on polymer nanocomposites with low content of environmentally harmful components and high physical and mechanical characteristics and improved functional properties. The development of materials using fillers of polymer matrices of micron and submicron level of dispersion to achieve a new level of performance has largely exhausted itself. New breakthrough solutions can be reached using the principles of nanotechnology, namely the transition to the nano disperse state of reinforcing components, the synthesis of which is very promising both theoretically and practically from the point of view of creating smart composite paints and varnishes [1-8] Such nano disperse particles are nanodiamonds - promising representatives of carbon nanostructures [9-13].

Nanodiamonds or ultrafine diamonds are a group of carbon nanostructures that have a crystal lattice characteristic of ordinary diamond: a planaxial class of cubic syngony, two face-centered Brave lattices, shifted relative to each other by 1/4 of the main diagonal, but the size of each to 10 nm. In dry form, nanodiamonds are light gray polydisperse powder.

It should be noted that the structure of nanodiamonds depends on the conditions of their synthesis, purification, and further processing. Thus, in the case of wet synthesis, the shape is close to spherical, while in dry synthesis, diamond nanocrystals close to the ideal structure are formed. Nanodiamonds, which are obtained during the explosion in a closed volume of condensed explosives with a negative oxygen balance, are a special type of diamond material. These are typical nanomaterials with an average grain size of 4 nm, which have a predominantly spherical shape, so they were used in this work.

Nanodiamonds have a three-layer structure which includes: a diamond core with a size of 4 to 6 nm, which contains 70 to 90% of carbon atoms in the sp3-hybridization state; a transition shell (intermediate layer) around the nucleus with a thickness of 0.4 to 1 nm, consisting of X-ray amorphous carbon structures and containing from 10 to 30% of sp2-hybridized carbon atoms; surface layer, in which, in addition to carbon atoms, there are other heteroatoms (N, O, H), which form a number of functional groups. Nitrogen gene atoms are fairly evenly distributed across all layers of nanodiamond.

The structure of the intermediate layer of the nanodiamond particle is inhomogeneous. The shell, which is directly on the border with the diamond core, consists of continuous layers of carbon in the form of onions, formed by groups of six atoms, the so-called hexagons. The transition shell also contains graphite-like monolayers concentrated in its peripheral parts and amorphous carbon.

A characteristic feature of nanostructures is that the carbon atoms in them have a coordination number inherent in ordinary diamond, equal to 4. Each carbon atom is surrounded by four other similar atoms. The extreme atoms on the surface have nothing to be surrounded by, and this leads to the creation of various uncompensated valences. Therefore, the properties of the surface layer of diamond differ from the properties of its inner layers. In the surface layer, carbon atoms can bind not only to each other but also to other heteroatoms: Nitrogen, Hydrogen and Oxygen, forming different functional groups. Functional groups in the surface layer were identified as hydroxyl, which is part of sorbed water and tertiary alcohols; amino groups in the composition of amides; carboxyl groups; carbonyl groups consisting of ketones, acid anhydrides, esters, and lactones. Bonds between Carbon and Hydrogen in the form of CH-, CH_2-, and CH_3-groups, as well as C-O-C bonds, have been identified.

A small particle has a larger surface area to volume ratio than a large particle. Accordingly, the role of surface atoms and groups in nanodiamonds increases significantly compared to ordinary diamonds. Thus, nanodiamond particles have the properties of diamond - strength, and stability, but acquire a number of unique properties: they are very small, they have a very large specific surface area and high surface energy, and due to the presence of functional groups, they can be modified, such as to "sew" various molecules, for examples like medicine and drugs. Today, among a large number of areas of the practical application of nanodiamonds, three main areas prevail: 70% of nanodiamonds are used for finishing polishing; 25% of nanodiamonds are used in electroplating; 5% - in oil compositions [14].

In the near future, extremely wide areas of application of nanodiamonds may be the production of polymer-diamond compositions, charge-transfer catalysts, and modified bio-resistant concrete [15].

Numerous studies have also shown the effectiveness of nanodiamonds in polymer composites and films based on polyfluorinated elastomers, perfluorinated hydrocarbons, polysiloxanes, polyisoprenes, butadiene-styrene rubbers, polyurethanes, and other substances. The introduction of nanodiamonds in general increases the elastic strength characteristics and provides in some cases the unique tribotechnical properties of polymers [16-20].

Particles of detonation nanodiamonds, obtained in non-stationary, extremely harsh conditions of an explosion, have not the usual smooth surface, but on the contrary - "bachromium" of functional groups. Hence the whole set of unpredictable properties and non-standard areas of their use. Nanodiamonds are being used in practice as selective adsorbents and catalyst carriers, and in the future nanodiamonds are planned to be used in the medical field, for example, for the targeted movement of drugs in the body and tissue regeneration.

The lack of information in the scientific and technical literature on systematic studies of the influence of nanodiamonds as modifiers in paint coatings determines the relevance of the work.

The aim of this work was to study the effect of nanodiamond particle additives on the physical-mechanical and optical properties of nanocomposite paints and coatings for further prediction of their use in various industries.

2 Materials and methods

Primal CM-219 EF water-dispersion acrylic dispersion (Rohm and Haas) was used to determine the effect of detonation nanocomposites on the physico-mechanical and optical properties of paint coatings. The compositions were prepared using a bead mill by dispersing water pastes with nanodiamonds (VPNA) and without nanodiamonds (VPD). Orotan 731 AER dispersant, cellulose and associative polyurethane thickeners, and Foamaster NXZ defoamer were used. As a coalescent - Texanol NX-795. Acrylic dispersion was added to the obtained water pastes at a speed of 280 rpm.

To study the effect of nanodiamonds on physical and mechanical properties of coating based on aqueous acrylic dispersions acrylic aqueous dispersions with nanodiamonds and without nanodiamonds were coated with steel plates to measure the resistance of coatings to impact, tin plates to determine the elasticity of coatings and glass plates and to determine the conditional hardness of coatings. The concentration of nanodiamonds varied from 0.2 to 0.5% as the most interesting in terms of their application technology and coating price.

After preparing samples physico-mechanical properties of paint coating were determined by standard methods.

The relative hardness is determined by the pendulum instrument (according to ISO 1522) by comparing the damping time of the pendulum oscillations on the sample with the "glass number".

Impact resistance of the coatings was determined (according to ISO 6272) using a device measuring the maximum height from which a load of 1 kg does not cause visible mechanical damage to the surface of the test plate with paint coating under a free fall of load.

Elasticity and bending strength of coatings (according to ISO 1519) were measured around a set of cylindrical rods with diameters from 1 mm to 32 mm. The method consists in determining the minimum diameter of a metal cylindrical rod the bending of which of the painted metal plate does not cause mechanical destruction or peeling of the paint film at a certain thickness.

The adhesion of paint coating was determined by the method of lattice cuts (according to ISO 2409).

The thickness of the coatings (according to ISO 2808) was 30 μm for all samples and was determined using a thickness gauge NOVOTEST TP-1 (L) for metals and dielectric products.

The wear resistance of the coatings was determined according to ISO 5470 by abrasion of the coating due to the mechanical action of a jet of quartz sand.

Conditional viscosity was measured using a viscometer type VZ-246 (ISO 2431).

The absorption efficiency of UV radiation was studied by changing the intensity of radiation of fluorescent pigments sensitive to different spectral ranges of UV radiation. The concentration of nanodiamonds in the suspension was 7% to obtain a more accurate value of the degree of absorption.

For this color and color coordinates of secondary radiation were determined using a portable spectrophotometer NS810. The task of experimental quantitative determination of pigment color is the calculation of color coordinates, chromaticity coordinates, color tone, color purity, and brightness in the standard colorimetric system XYZ. The obtained values allow us to graphically represent the color in Cartesian coordinates x and y on a color graph.

In addition to a certain color by color coordinates X, Y, Z, color coordinates x, y and z in combination with the color coordinate Y, it is possible to determine the color by color tone λ, pure color P, and brightness Y. The color tone is characterized by the dominant wavelength λ, ie the co-wavelength corresponding to the maximum on the reflection spectrum of the sample. It can be determined on a color chart by given or calculated chromaticity coordinates x, in this sample. The purity of color P is determined by the ratio of photometric brightness of monochromatic radiation and total brightness of radiation. On the color graph, the value of color purity P is determined by the ratio of the distance from the white point to the point with the coordinates of the chromaticity of the sample (x, y) and the length of the segment drawn to the line of spectral colors. Brightness or brightness (L) characterizes the amount of light reflected by the sample.

As a result, the research methodology made it possible to study the most important technological parameters of both the suspension and the finished coating in the most important range of filler concentrations.

3 Results and discussion

The results of the influence of detonation of nanocomposites on the physical and mechanical properties of water-dispersion paint coatings for the optimal composition (0.3% nanodiamonds) which are given in Table. 1. show a significant increase in the conditional hardness of the coating (almost 60%) and wear resistance (almost 140%).

Wherein the viscosity of the aqueous acrylic dispersion was slightly lower than the viscosity of the aqueous acrylic dispersion with nanodiamonds and was 44 s and 48 s, respectively (at 20 ± 0.5 °C).

Table 1. Physico-mechanical properties of pure acrylic dispersion (VP) coatings and coatings based on compositions of aqueous acrylic dispersion with nanodiamonds (VPND).

Property	VP	VPND
Conditional hardness of coatings, un.	0.38	0.61
Impact resistance of coatings, cm	50	50
Resistance of coatings to bending, mm	2	2
Adhesion of coatings, points	0	0
Wear resistance kg/kg	3.80×10^{-7}	1.58×10^{-7}

A more detailed study of the temperature dependence of the conditional hardness of samples based on an aqueous acrylic dispersion and an aqueous acrylic dispersion with the addition of nanodiamonds in the range from 0.2% to 0.5% (Fig. 1) revealed an extreme nature of the dependence on the concentration of nanodiamonds.

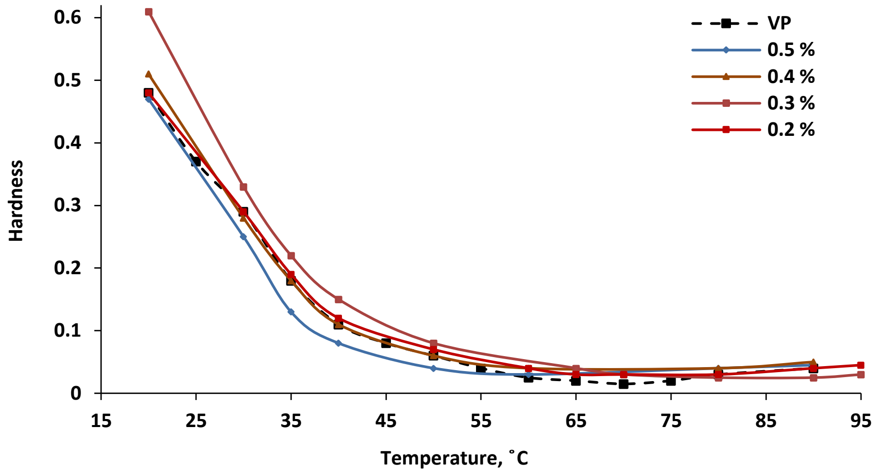

Fig. 1. Temperature dependences of the conditional hardness of coatings depending on the content of nanoparticles.

For all samples there is a single type of dependence of hardness on temperature, which is characterized by a minimum at temperatures of 50-90 °C. More clearly the differences in the change in hardness from temperature are found in the logarithmic coordinates for hardness, which are shown in Fig. 2.

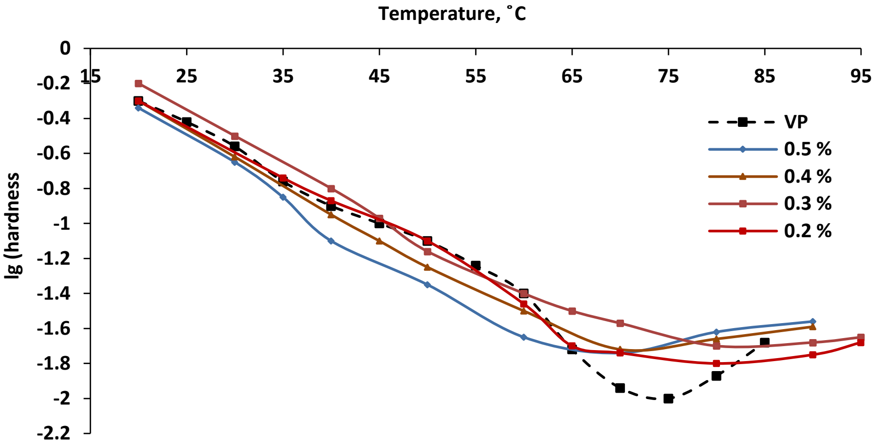

Fig. 2. Logarithmic dependence of the hardness of coatings on the content of nanodiamonds.

The results showed that the introduction of nanodiamonds in the amount of 0.5% leads to a decrease in conditional hardness at medium temperatures (30-70 °C), the introduction of nanodiamonds of 0.3% increases the hardness for the entire temperature range and in the temperature range of 60-80 °C any amount of nanodiamonds increases the hardness of the coating.

This dependence of hardness on from the concentration of nanodiamonds and temperature becomes even more obvious when displayed in relative units (relative to the sample without nanodiamonds) (Fig. 3).

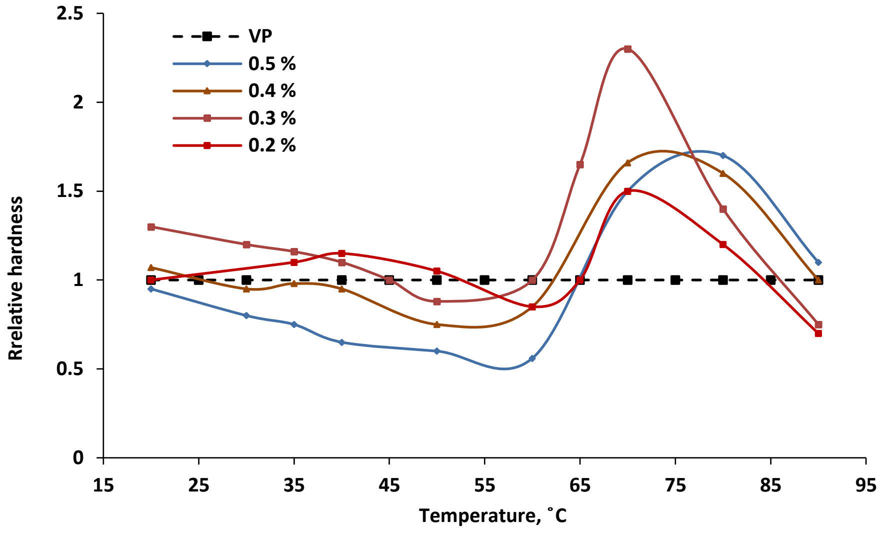

Fig. 3. Temperature dependence of hardness in relative units (in relation to the sample without nanodiamonds)/

The additive has the greatest effect in the amount of 0.3%, and when it is made, it is possible to increase the hardness not only at temperatures of 70-80 °C, but also when the temperature drops below 20 °C. The dependence of the maximum deviations for the three temperature ranges on the amount of additive shows that for concentrations less than 0.4% increase the hardness reaches 230% relative to the pure material, and even at average temperatures the decrease in strength does not exceed 10%. Nano disperse diamond has the greatest effect on hardness at a temperature of 70-80 °C.

The experimental results obtained made it possible to create a fairly simple mathematical model that makes it possible to predict the hardness of coating using these two parameters:

$$H = \left(0.962 \cdot \frac{T+273.15}{273.15}\right)^{-20.75} + \left(\left(0.0573 - 0.117 \cdot |C - 0.3|\right) \cdot \frac{T+273.15}{273.15}\right)^{14.9} (1)$$

where H – hardness, units; T – temperature, ℃; C – concentration of nanodiamond in suspension, % mass.

As mentioned above, the analysis of the literature indicates the feasibility of studying the absorption of electromagnetic radiation in the ultraviolet region of the spectrum by nanodiamonds. To do this, fluorescent pigments were placed under the film of an acrylic dispersion with nanodiamonds with a D65 light source located above it.

Three samples of luminescent pigments of yellow, green, and red color were taken, for which color coordinates, chromaticity for XYZ, CIELAB colorimetric system and dominant wavelength, saturation and color brightness were determined. The measurement data for pigment samples without a film and pigments with a film with nanodiamonds are given in Table. 2.

Table 2. Color parameters of the studied pigments under UV radiation.

Type of sample	XYZ	CIELAB	λ, P, Y
Red with ND	X=4.1058 Y=4.9670 Z=5.9987	L=22.85 A=-2.4 B=5.14	λ=525, P=5%, Y=4.6771
Red	X=5.1421 Y=5.7497 Z=6.7823	L=27.91 A=-0.17 B=-2.14 ΔE=9.15	λ=525, P=10%, Y=5.7497
Yellow with ND	X=26.2291 Y=25.0617 Z=38.1268	L=57.14 A=7.77 B=-11.87	λ=565, P=22.22%, Y=25.0617
Yellow	X=29.1335 Y=28.5971 Z=40.1755	L=60.42 A=5.1 B=-8.63 ΔE=5.5	λ=565, P=40%, Y=28.5971
Green with ND	X=11.6266 Y=13.8998 Z=23.3076	L=44.04 A=-12.72 B=-13.49	λ=568, P=5%, Y=13.8998
Green	X=16.5657 Y=18.3176 Z=26.0161	L=49,88 A=-6,83 B=-7.88 ΔE=10.01	λ=568, P=30%, Y=18.3176

The brightness of fluorescent pigments of red, yellow, and green colors exposed to UV radiation compared to the brightness of pigments under an acrylic-coated filter with nanodiamond nanoparticles for a D65 light source in the CIELAB colorimetric system increased from 22.85 to 27.91, from 57.14 to 60, 48 and from 44.04. The calculated differences in color ΔE in the CIELAB system for pigment samples and samples with nanodiamond filters indicate a significant effect of nanodiamonds included in the coating composition on pigment colors due to a decrease in the effect of ultraviolet radiation on the fluorescence of pigment samples.

4 Conclusions

As a result of studying the effect of detonation nanodiamonds on the physical-mechanical and optical properties of water-dispersion paints, it was found that the introduction of nanodiamonds leads to significant increase in the conditional hardness of the coating (almost 60%) and wear resistance (almost 140%) and almost does not change the viscosity of the suspension.

It was determined that the optimal amount of nanodiamonds is 0.3%, providing a 2.4-fold increase in the hardness of the coating, and the most effective effect of nanodiamond additives on the hardness of coatings for temperatures of 60-80 °C.

Based on the results of the experiments, a simple mathematical model was proposed for the dependence of the coating hardness on the concentration of nanodiamonds in suspension and temperature.

As a result of the research, the possibility of creating an effective UV radiation filter based on paint coatings with the inclusion of nanodiamonds has been proved.

Therefore, the results of the study make it possible to recommend the use of detonation nanodiamonds in various industries both to improve the performance properties of paint coatings and to create new optical materials in the field of UV radiation.

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