Nano World Journal

https://doi.org/10.17756/nwj.2023-115

Research Article

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Studying the Effect of Adhesion and Biological Properties for ZnO and TiO_2/PVA Nanocomposite on Activity of Paints and Epoxy by Accelerated Weathering Tester

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Received: April 12, 2023
Accepted: May 04, 2023
Published: May 11, 2023

Citation: Al-Dharob MH, Odah JF, Hamad AA, Younis A, Hussain N, et al. 2023. Studying the Effect of Adhesion and Biological Properties for ZnO and TiO_2/PVA Nanocomposite on Activity of Paints and Epoxy by Accelerated Weathering Tester. *Nano World J* 9(2): 37-42.

Published by United Scientific Group

Abstract

Adhesion, biological properties of Iraqi coatings were developed by using ZnO (Zinc oxide) and TiO_2 (Titanium dioxide) NPs (nanoparticles) with PVA (polyvinyl alcohol). Iraqi dyes produced in the Modern Paints Company such as (gray food epoxy, for the inside drinking water tanks epoxy, lead food epoxy and transparent food epoxy primer) suffer from poor adhesion on a gypsum (Bork) piece, peeling ability, and low biological activity as a function of time. Experimental results of the coated gypsum (Bork) piece with these un-developed coating shows low adhesion force for all samples arrange from (11 N/m^2 for hospital dye to 134 N/m^2 for food grade transparent epoxy primer), while the developed coating have values range from (95 N/m^2 for gray food epoxy to value of 160 N/m^2 for white hospital epoxy). Furthermore, the adhesion force after time-acceleration weathering show also high adhesion force for developed coating as compared with original coating where the values range for undeveloped coating were (42 N/m^2 for white hospital epoxy and 113 N/m^2 for hospital dye) while the developed coating range were (52 N/m^2 for food grade transparent epoxy primer to 142 N/m^2 for hospital). The Biological efficiency as anti-parasitic against (*Escherichia coli* and *Staphylococcus aureus*) for the sample oil food dye shows non biological efficiency before additive, while this sample shows a biological efficiency after additive and after acceleration time by using time-acceleration weathering test over a period of more than six months. As a result, the additive of ZnO and TiO_2/PVA nanocomposite show the development of some Iraqi coating by the increment in adhesion force for the samples directly and after six months also show a biological efficiency for oil food dye.

Keywords

Local paints, Zinc oxide, Titanium dioxide, Nanoparticles, biological efficiency, Adhesion

Introduction

In both clinical and industrial settings, bacteria are typically found on and around surfaces. In hospitals, prevention and treatment of microbial infections are of paramount importance. The surfaces of devices are often coated with antimicrobial agents to reduce the risk of infection following implantation. Depending on whether antibacterial agents are delivered on a local level, they can be either passive or active. To prevent bacteria from adhering and even kill them on contact, passive coatings can be used. The most promising are metallic NPs, which exhibit great antibacterial properties due to their extensive surface area to volume ratio. However, research enthusiasm is ebbing and flowing due to the evolution of microbial resistance to metallic particles, anti-toxins, and the development of safe strains [1].

Nanomaterials are increasingly being used in many different areas, including energy production, environmental applications, biomedicine, and biotechnology, and as a result are showing up in a growing number of consumer goods. The fundamental understanding of combustion science and engineering can be successfully applied to the primary areas of inquiry in the nanomaterial field, such as the synthesis of NPs with tailored properties and their assembly into useful devices and coatings [2].

ZnO NPs are one of the most widely used nanomaterials, found in products as diverse as sunscreen and textiles [3-6] due to their exceptional physicochemical properties. ZnO NPs have been found to be effective antibacterial agents against a wide variety of bacteria, including spores, of both the Gram-positive and Gram-negative varieties. The advantages of ZnO NPs over other NPs include their low toxicity, biological compatibility, bioactivity, and chemical stability [7]. These properties give ZnO NPs broad antimicrobial activity against a variety of microorganisms [8, 9], this includes, but is not limited to, *E. coli, S. aureus, Pseudomonas aeruginosa, Bacillus subtilis*, and the M13 bacteriophage.

Recent years have seen a rise in interest in nanocomposite materials, both in the classroom and the workplace [10]. Due to their nanoscale dimensions, vast specific surface areas, quantum confinement effects, and robust interfacial processes, polymeric materials can benefit from the incorporation of a scant nano load [11].

For its production, the acetate groups in polyvinyl acetate are either partially or completely hydrolyzed away, leaving behind the linear synthetic polymer known as polyvinyl alcohol (PVA). PVA is a biodegradable polymer that can be dissolved in water; when combined with ZnO NPs, the resulting nanocomposite exhibits enhanced electrical, mechanical, and optical properties. This non-toxic biodegradable nanocomposite can replace plastics and other less-than-ideal packaging options for food products. The mechanical, chemical, and physical properties of PVA are all affected by its degree of hydroxylation [12, 13]. PVA's mechanical strength, moisture and oxygen barrier properties, and surface hydrophobicity were all improved by the addition of nano-ZnO [14].

To measure the adhesive strength, it is necessary to separate the coating sample from the substrate (Borax). As a rule, a pull-off test is used to evaluate the tensile strength of an adhesive. Improvements in adhesive strength can be explained by an increase in intermolecular forces between the substrate (Primarily borax) and the paint. After extensive research, scientists settled on a ZnO/PVA composition that has low strength and can be easily torn off or removed once the coatings have dried [15]. To increase the biological efficiency against microbial, overcome the problem of weak adhesion strength of ZnO/PVA alone, and guarantee the continuity of biological efficiency for a long time without being affected by weather factors, this paper's studies show the effect of ZnO/PVA nanocomposite additive in painting applications. Properties of TiO$_2$ NPs include bactericidal, photocatalytic activity, safety, and self-cleaning [16-18]. In this search the additive of ZnO and TiO$_2$/PVA nanocomposite show increasing in adhesion force for all samples that was used and furthermore show a good biological efficiency for anti-parasitic oil food dye, these results can be a method for developing dyes that need high adhesion ability and weather conditions such as street and road coatings.

Mechanism of antimicrobial activity of ZnO NPs

ZnO NPs may play a role in antibacterial activity by accumulating in the outer membrane or cytoplasm of bacterial cells, where they would trigger Zn^{2+} release, leading to membrane disintegration, protein damage, and genomic instability, all of which would kill the bacterial cells [19-21].

Although the correct toxicity regimen is not very clear and remains controversial. However, there are studies and research indicating the mechanism of killing microbes using ZnO NPs, which requires a study of the mechanics of the action of these NPs on bacteria. Specific and recorded killing mechanisms include ZnO NPs directly attach to cell walls and thus destroy those cells [22], or through the release of Zn ions as antibodies [23], or the formation of oxygen ions. Effective [24]. For example, the formation of highly reactive groups like OH^-, H_2O_2, and O_2^{-2} is shown below. The presence of an electron gap pair (e-h^+) in ZnO. ZnO has an energy gap that separates H_2O molecules into OH and H^+. This results in the formation of free radicals (O^{-2}), which react with H^+ to form free radicals (HO_2), which then collide with electrons to form hydrogen peroxide (HO_2). Afterwards, they combine with hydrogen ions to form H_2O_2 molecules. Permeation of cell membranes by H_2O_2 and subsequent bacterial death is a well-documented phenomenon.

$ZnO + hV\ e^- \rightarrow h^+,\ h^+ + H_2O.OH + H + e^- + O_2 \rightarrow \bullet O^{-2};\ \bullet O_2 + H^+ \rightarrow HO_2 \bullet HO_2 \bullet + H^+ + e^- \rightarrow H_2O_2$

In addition to the production of reactive oxygen species (ROS) during the interaction of metal oxide with bacteria, other mechanisms contribute to the bactericidal activity of ZnO NPs. The amount of ROS produced is proportional to the ion release rates of the metal oxide used in the NP's synthesis [25, 26].

Mechanism of antimicrobial activity of TiO2-NPs

TiO$_2$ NPs antimicrobial activity is commonly attributed to its ability to generate highly oxidizing ROS in the presence of oxygen (O_2), ROS which then kill bacteria in a variety of ways [27-29].

Experimental Part

4 gm of PVA was dissolved in 100 ml of deionized water using a magnetic sterilizer (Magnetic sterilizer /IKA RH basic 2 Germany) for 1 hour at 60 °C, followed by the addition of 0.6 gm of ZnO NPs with a stirrer for 1 hour at 60 °C. The temperature of this solution was allowed to drop to room temperature. Other samples were also prepared in the same way, using ZnO and TiO$_2$ in a 1:1 ratio, with the same weights listed above. Following this, 80 ml of each paint type manufactured by Modern Paint Industries Company-Iraq were mixed

with 20 ml of the final solution as shown below.

Anti-parasitic oil food dye A-1008.

Hospital dye D-9058.

White Hospital Epoxy D-5800SFFA.

Epoxy to paint the inside of drinking water tanks D-5547A-91.

Gray Food Epoxy D-5544 SFA-12.

Food grade transparent epoxy primer G-5900.

SEM images of commercial NPs showing irregular shapes (irregular ovoid, elongated, and circular) and sizes for both ZnO and TiO_2 NPs with irregular shapes being the main shape for both (Figure 1 and figure 2). The SEM images also show the average crystal size, which indicates that TiO_2 NPs are smaller than ZnO NPs. Mean particle size distributions were found to range from 25 to 100 nm which correspond to the manufacturer's specifications, which indicate that particles should have a size of less than 100 nm.

The modified paint was stirred for 5 min, then a piece of borax was painted in the mold of the cohesion and time-acceleration weathering devices, where it was rolled on three layers and left to dry, and then tests for the lasting adhesive tester/posi test AT-M USA, Accelerated weathering tester /model QUV/ Se USA and test of biological efficiency against (E. coli and S. aureus) bacteria were carried out.

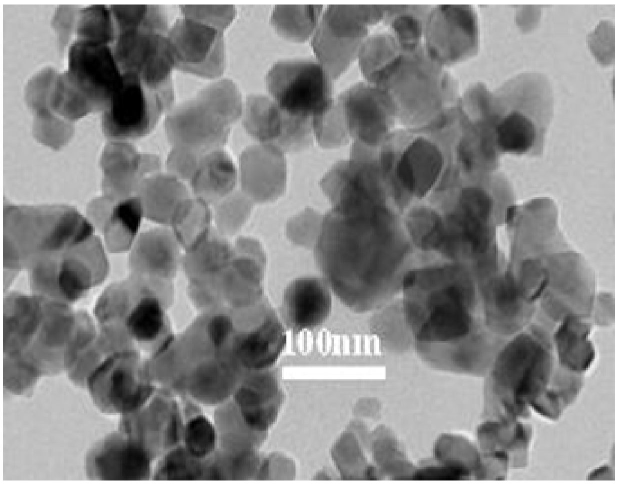

Figure 1: ZnO NPs from US research nanomaterial, Inc USA [29].

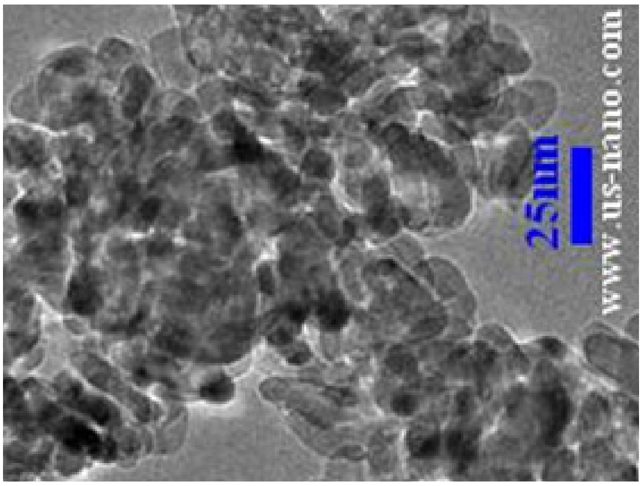

Figure 2: TiO_2 NPs from US research nanomaterial, Inc USA [29].

Results and Discussion

Table 1 represents the adhesion force for coatings and epoxy which is used to paint the walls and floors of the hospitals before and after adding ZnO NPs blended with PVA polymer. These results were before weathering acceleration.

Form figure 3 and table 1 shows almost samples high adhesion force after adding ZnO/PVA nanocomposite, one can conclude that the adhesion force was increased for samples (A-1008, D-5544SFA, D-5547A-9101, D-9058, and D-5800) with a ratio reach to (44%) for A-1008 paint while the adhesion force was increased with more than (10) doubles for hospitals' paint (D-9058). This significant increase in adhesion force after adding ZnO/PVA may be attributed to the polymer ability to increasing to the correlation force between the paint's molecules and the painted walls. Also, the polymer adding leads to forming new bonds between the original molecules of the paint, these bones did not exist before adding the polymer. ZnO NPs adding will play an important role in adhesion force increment, it will decrease the inter-distances between the paint molecules and create new bonds within these molecules. On the other hand, ZnO NPs will fill the holes and gaps that are already found in the paint and between the paint and the floor or wall.

From figure 4 and table 2, the adhesion force for the samples after addition of nanocomposite was also higher than for the samples without addition after six months of weathering acceleration about (16% - 55%). This gives an indication that

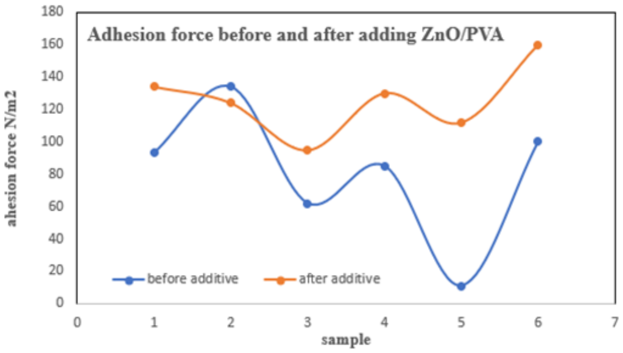

Figure 3: Adhesion force before and after adding ZnO/PVA.

Table 1: Adhesion force before and after adding ZnO/PVA.

S. No.	Sample	Adhesion force before adding ZnO/PVA (N/m^2)	Adhesion force after adding ZnO/PVA (N/m^2)
1	A-1008	93	134
2	G-5900	134	124
3	D-5544SFA	62	95
4	D-5547A-9101	85	130
5	D-9058	11	112
6	D-5800	100	160

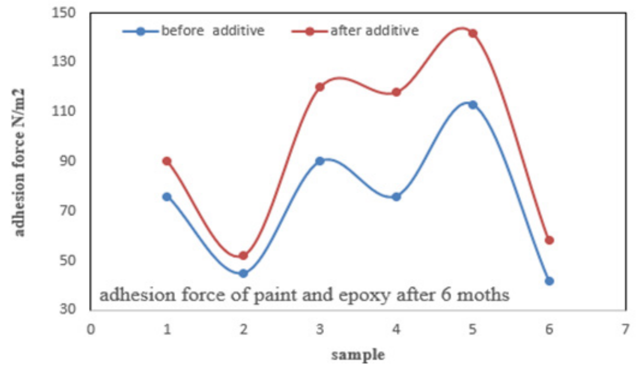

Figure 4: Additive effect on paint and epoxy after 6 months.

Table 2: Adhesion force before and after adding ZnO/PVA with six months weathering acceleration 60 °C and 61 of humidity.

S. No.	Sample	Adhesion force before adding ZnO / PVA (N/m^2)	Adhesion force after adding ZnO/PVA (N/m^2)
1	A-1008	76	90
2	G-5900	45	52
3	D-5544SFA	90	120
4	D-5547A-9101	76	118
5	D-9058	113	142
6	D-5800	42	58

the paint will be affected with very low ratio by the environmental (weather) conditions as a result due to forming new intermolecular strong bonds by adding ZnO/PVA composite to the original paint or epoxy. Furthermore, Hospital dye D-9058 shows the best effect of additive to the adhesion force as compared with other samples.

The biological efficiency of the samples has been obtained, for the all-control samples there weren't any biological efficiency before additives of (ZnO and TiO_2/PVA nanoparticle solution). Figure 5a and 5b show the biological activities of paints with adding ZnO/PVA before and after time acceleration respectively on (*E. coli* and *S. aureus*). While figure 6 shows the biological efficiency of the sample (Anti-parasitic oil food dye A-1008) after adding ZnO/TiO_2 with ratio 1:1, it is clear that the inhibition zone of this sample is about 10 mm against (*E. coli*).

Table 3 show the biological efficiency of the painting before and after additive also its show the effect of nano-additives on biological efficiency as a function of accelerated weathering tester, it's clear that it was efficient against gram negative *E. coli* and gram-positive *S. aureus* for two samples (Anti-parasitic oil food dye A-1008 and White Hospital Epoxy D-5800SFFA), this behavior of these dye and epoxy can be explained due to the mechanism of ZnO NPs against bacteria.

Figure 7 explain the stages and steps of conducting the research, which include conducting adhesion and biological activity tests without additives on the one hand and with additives on the other hand and repeating these tests after 6 months have passed using Accelerated Weathering Tester.

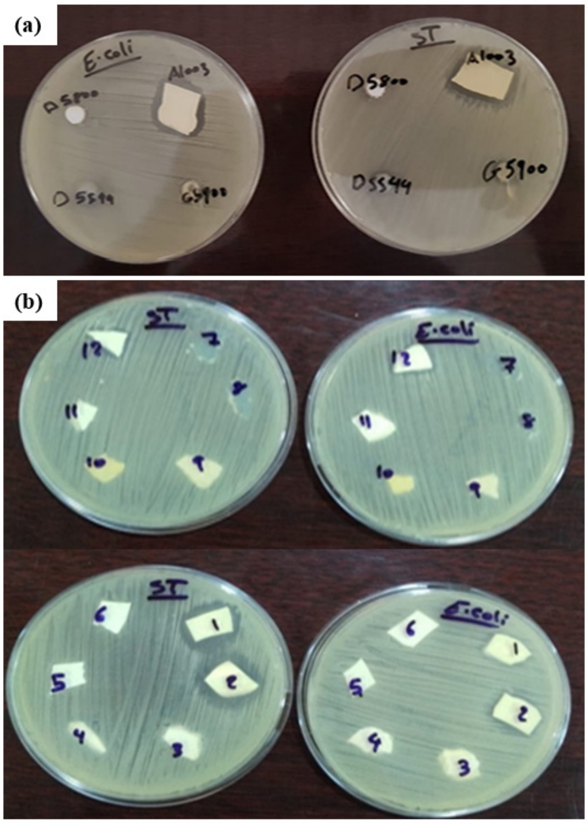

Figure 5: Biological activities of the paints on the with adding ZnO/PVA before time acceleration **(a)** and after time acceleration **(b)**.

Figure 6: Biological activities of the paints on the with adding ZnO-TiO_2/PVA.

Conclusion

Additives with 7 wt.% ZnO, TiO_2/PVA nanocomposite concentration improved the adhesive's mechanical properties (bond strength and dentin interaction) of some Iraqi dyes produced in the Modern Paints Company such as (Anti-parasitic oil food dye A-1008 and White Hospital Epoxy D-5800SFFA) with ratio 1:5. Also can be effective for a long period as

Table 3: Biological activities of the mentioned paints on (*E. coli* and *S. aureus*).

S. No.	Sample	Code	Biological eff. before additive	Biological eff. after additive	Biological eff. after time acceleration
1	A-1008	1 before time acceleration	Not effective	Effective	Effective
		2 after time acceleration	Not effective	Effective	Effective
2	Hospital dye D-9058	3 before time acceleration	Not effective	Not effective	Not effective
		4 after time acceleration	Not effective	Not effective	Not effective
3	Epoxy to paint the inside of drinking water tanks D-5547A-91	5 before time acceleration	Not effective	Not effective	Not effective
		6 after time acceleration	Not effective	Not effective	Not effective
4	Gray Food Epoxy D-5544 SFA-12	7 before time acceleration	Not effective	Not effective	Not effective
		8 after time acceleration	Not effective	Not effective	Not effective
5	Food grade transparent epoxy primer G-5900	9 before time acceleration	Not effective	Not effective	Not effective
		10 after time acceleration	Not effective	Not effective	Not effective
6	White Hospital Epoxy D-5800SFFA	11 before time acceleration	Not effective	Not effective	Not effective
		12 after time acceleration	Not effective	Effective	Effective

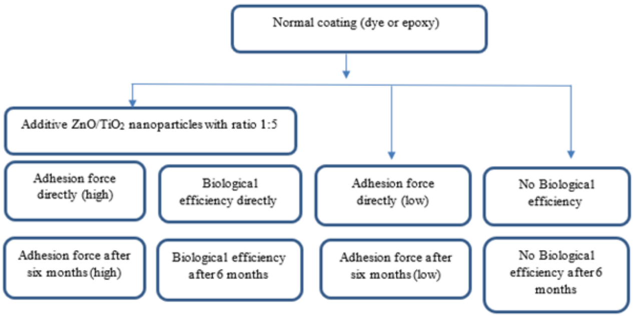

Figure 7: Schematic diagram for the coating (dye and epoxy) adhesion and biological properties with and without additive of ZnO-TiO_2/PVA nanocomposite.

compared with original paints and epoxy. Furthermore, these additives show good biological efficiency against gram-negative *E. coli* and gram-positive *S. aureus* for Iraqi dyes (Anti-parasitic oil food dye A-1008). This research obtained patent No. 7348 on date 5.22.2022 Issued by the Iraqi Central Agency for Standardization and Quality Control.

Acknowledgments

Mohammad H Al-Dharob, Jafer Fahdel Odah, Ammar Abdullah Hamad, Ahmed Younis, Nada Hussain, Ruba Abdul Rasul Ahmed and Raya Abdul Ameer, acknowledges College of Science, Al-Karkh University of Science, Baghdad, Iraq and Ministry of Industry and Minerals, Industrial Research and Development Authority, Baghdad, Iraq

Conflict of Interest

On behalf of all authors, the corresponding authors states that there is no conflict of interest.

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