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CHARACTERIZATION OF PHOTOCATALYTICALLY ACTIVE COATINGS BASED ON TiO_2/Zn-Al LAYERED DOUBLE HYDROXIDE ON CERAMIC TILES

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The self-cleaning function (photocatalytic activity and surface hydrophilicity/hydrophobicity) is of great importance for ceramic tiles from both economic and environmental point of view. This research is focused on the preparation of suitable photocatalytic suspensions studying the influence of the photocatalyst powder amount and the molecular mass of polyethylene glycol (PEG) on the self-cleaning properties of the suspensions deposited on the ceramic tile surface. Photocatalysts based on Zn-Al double layered hydroxides with TiO_2 as active component, were synthesized and used for the preparation of the suspensions. The coated tiles prepared using smaller photocatalyst amount and the highest investigated molecular mass of PEG (PEG 4000) showed the highest photocatalytic activity in the Rhodamine B degradation reaction, as well as the appropriate surface properties.

KEY WORDS: self-cleaning, photo-induced hydrophilicity, surface properties, photocatalytic active suspension, TiO_2/Zn-Al layered double hydroxide

INTRODUCTION

Building materials are constantly exposed to the environmental factors, pollutants of inorganic and organic origin, as well as microorganisms, which are significantly contributing to their deterioration. The deterioration is irreversible, involving both chemical and physical process, always starting at the material surface and penetrating gradually into the material. The consequences of the deterioration and damage of building materials could be avoided by their adequate protection. The application of coatings can decrease the negative action of the various environmental pollutants by minimizing their direct contact with the surface of the building material. Different types of coatings with additional functions have been developed (1). The main purpose of the coating application is to change the surface properties in order to prolong the material durability by adding some new properties. One of the most convenient and environmental friendly way to perform this is the development of multifunctional self-cleaning and photocatalytically

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active materials and their application on large surfaces of building materials exposed to negative actions of environmental factors.

Synthesis, examination and application of new, multifunctional materials with self-cleaning and photocatalytic properties is recognized by many researchers (2-6). The most widely used photocatalyst is TiO_2 (7). One of the most interesting aspects of TiO_2 is that the photocatalysis and hydrophilicity can take place simultaneously on the same surface even though the mechanisms are completely different (8). The photocatalytic phenomenon has been studied intensively for a number of years by many groups, and it is well understood (9, 10). After light irradiation of TiO_2, the photo-generated electrons and holes react with molecular oxygen (O_2) and water to produce superoxide radical anions ($O_2^{\bullet}$) and hydroxyl ($OH^{\bullet}$) radicals, respectively. Both of these reactive radicals participate in decomposition reactions of organic compounds (11). On the other hand, OH^- groups can trap more photo-generated holes and improve the separation of electrons and holes (12), which results in the enhancement of the photocatalytic effect/activity. As for the hydrophilicity phenomenon, the photo-induced electrons and holes react in a different way. The electrons tend to reduce the Ti^{4+} cations to the Ti^{3+}state while the holes oxidize the O_2^- anions and, as a consequence, oxygen atoms are ejected, creating oxygen vacancies. Water molecules from the environment then occupy these oxygen vacancies, producing adsorbed OH^-groups, which tend to make surface more hydrophilic (8).

The problems regarding possible health issues of using nanosized TiO_2 could be eliminated by using microsized TiO_2 (13) or by suitable immobilization of TiO_2 particles onto a photocatalyst support, which can prevent particle aggregation, improve photocatalytic activity, and, what is very important, improve the compatibility with porous ceramic tile. Those were the main reason for the development of an inorganic-inorganic nanocomposite photocatalyst based on layered double hydroxides (LDHs) associated to TiO_2. The LDHs are a class of synthetic two-dimensional nanostructured anionic clays, with advantageous textural, acid-base and redox properties, which can enable a wide range of applications (14). In order to design protective coatings suitable for porous building materials and analysis of the materials surface properties before and after the application of newly designed photacatalytic active, hydrophilic TiO_2/ZnAl LDH based coating was performed and the results of the investigation are presented in this work. The TiO_2/Zn-Al nanocomposite powder with proven photocatalytic properties (15) was used for the preparation of the suspension. Zinc was selected as a constituent LDH metal because of its photocatalytic and antimicrobial activity and proven contribution to the overall activity of the novel TiO_2/Zn-Al nanocomposite. In this study TiO_2/Zn-Al nanocomposite powder was synthesized and used for the development of the suspension which can improve compatibility between the coating and the ceramic tile. The polyethylene glycols (PEG) of different molecular mass were investigated as binder for the preparation of photocatalytic active suspension with the aim to attain stable suspension, decrease agglomeration of TiO_2 particles, not influencing at the same time the porosity of the ceramic tile during the formation of a mesoporous coating.

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EXPERIMENTAL

Synthesis of photocatalytic powder and the suspension preparation

The Zn-Al LDH was synthesized by coprecipitation method at a constant pH (15). The chosen metal precursors, $Zn(NO_3)_2 \cdot 6H_2O$ and $Al_2(NO_3)_3 \cdot 9H_2O$ were continuously (4 cm^3 min^{-1}) added at constant temperature (40°C) and by simultaneous addition of 0.67 M Na_2CO_3 and 2.25 M NaOH solution the pH was maintained constant (9–9.5). The precipitates were aged for 15 h, washed with water until the pH 7, dried for 24h at 100°C, and calcined at 500°C in air for 5 h. The wet impregnation process was carried out using the TiO_2 suspension (VP Disp.W 2730 X Degussa) that was diluted (3 mass%) in a 0.67 M Na_2CO_3 base solution and loaded onto the calcined Zn–Al LDH powder. The excess water was removed in a rotary vacuum evaporator at 55°C. The impregnated sample was dried for 12 h at 100°C, after which the TiO_2/Zn-Al LDH nanocomposite powder was obtained.

The TiO_2/Zn-Al LDH nanocomposite suspension that was used for coatings was prepared by the sol-gel method with H_2O_2 solution (16). The suspensions were prepared using Dissolver DISPERMAT® LC30 instrument with homogenizer. During the suspension preparation, 0.1 mass% of PEG of different molecular mass (PEG 4000, PEG 2000, PEG 600) was added as well. The suspensions with PEG 4000 were prepared with different amounts of the photocatalytic powder (1 mass% and 2 mass%). The denotation of the suspension samples and suspension preparation parameters are given in Table 1.

Table 1. Denotation and preparation parameters of the developed suspensions

Denotation of the suspension	Amount of photocatalytic powder (mass %)	PEG molecular mass (g/mol)
S2–PEG 4000	2	4000
S1–PEG 4000	1	4000
S1–PEG 2000	1	2000
S1–PEG 600	1	600

The suspension was deposited on the ceramic tiles by spray technique (p = 6.5 bar, nozzle diameter of 0.6 mm) with three layers applied. The coated samples were denoted similar as the suspensions: C2–PEG4000, C1–PEG4000, C1–PEG2000, C1–PEG600.

Particle size distribution of the prepared suspensions was determined on a Malvern Instruments, zeta-nanoseries, NanoZS zeta sizer. The measurements parameters were as follows: refraction index 1.55 and the absorption index 0.25. The suspensions were diluted up to 0.1 mass % of the solid phase.

The surface roughness of the reference tile and of the coated tiles was determined using Surtronic 25, Taylor Hobson precision device, and the obtained data were calculated following the ISO 4287 standard. The surface roughness was evaluated based on the R_a parameter, which represents average roughness values obtained with a 4 mm linear probe length.

Hydrophilicity assessment was performed by measuring the contact angle between the experimental fluid (water) and the coated surfaces of the investigated ceramic tiles using Surface Energy Evaluation System, Advex Instruments. The liquid drops, of about 5 μl in volume, were deposited on the tile surface using a micro-syringe. The measurements of the initial contact angle (θ_{ci}, after 1s) and the static contact angles (θ_{cs}, after 20s) were performed at five different points for each of the three specimens of the examined materials. Each droplet deposited onto the surface was measured five times.

The photocatalytic behavior of the coated samples was investigated by monitoring the change of Rhodamine B (RhB) concentration under UV/VIS irradiation (17). The photocatalytic activity was evaluated from the RhB removal efficiency. In order to saturate the samples before the photocatalytic assessment, a preabsorption test with RhB solution (10 ppm dm^{-3}, for 24h) was carried out. After the preabsorption, the RhB solution was replaced with a fresh solution. The samples were irradiated for 30, 90, 150 and 210 min. (EVERSUN lamp, intensity of UV-A and visible light spectra were 0.8 mW cm^{-2} and 0.3 Wm^{-2}, respectively). A UV/VIS spectrophotometer (EVOLUTION 600 spectrophotometer) was used to carry out the monitoring of the RhB concentration change at the major absorption peak (λ = 554 nm) and expressed by the following equation:

$$A(\%) = [(C_0 \cdot C)/C_0] \cdot 100$$

where C_0 is the RhB concentration of the sample in the dark at a defined time and C is the RhB concentration of the sample under UV/VIS light at the defined time (15).

RESULTS AND DISSCUSION

Suspension particle size distribution

The results of the particle size distribution measurements are presented in Figure 1. The influence of the amount of photocatalytic powder on the particle size distribution for the suspensions made with PEG 4000 is presented in Figure 1a. Both suspensions have a wide distribution of microsized particles. The suspension with the smaller amount of photocatalytic powder (S1–PEG 4000) has smaller particles with the dominant fraction of particles with average diameter from 1300 nm and a small fraction of particles with average diameter of 300 nm. The suspension with the larger amount of photocatalytic powder has a monomodal particle size distribution with particles having average diameter of 1700 nm. Since the suspension with the smaller amount of photocatalyst (1 g) has smaller particles, this smaller amount of photocatalyst was selected for further suspension preparation study with different PEG having smaller molecular mass. The influence of the different PEG molecular mass on the particle size distribution of the suspensions is presented in Figure 1b. The suspension prepared with the PEG of the smallest molecular mass (PEG 600) has a distinct bimodal particle size distribution of micro-sized particles with the dominant fraction of particles having average diameter of 1300 nm and with the second fraction of larger particles having average diameter of 5400 nm. The suspension S1–PEG 2000 possesses a wide trimodal particle size distribution with the most intensive wide peak at 1700 nm having a wide „shoulder“ at 300 nm and another peak at 5300 nm, while the suspension S1–PEG 4000 possesses the smallest particles in the studied series

of suspensions prepared with different PEG. The suspension S1–PEG 4000 does not have a fraction of larger particles with diameters around 5000 nm, but only a dominant fraction of particles with average diameter of 1300 nm and a small fraction with 300 nm. Since smaller particles are preferable for the stability of suspension, the suspension prepared with the PEG of the highest molecular mass is favorable for the preparation of suspensions. Nevertheless, all of the developed suspensions have particles that are microsized eliminating the health issues which occur in the case of usually used nanosized suspensions.

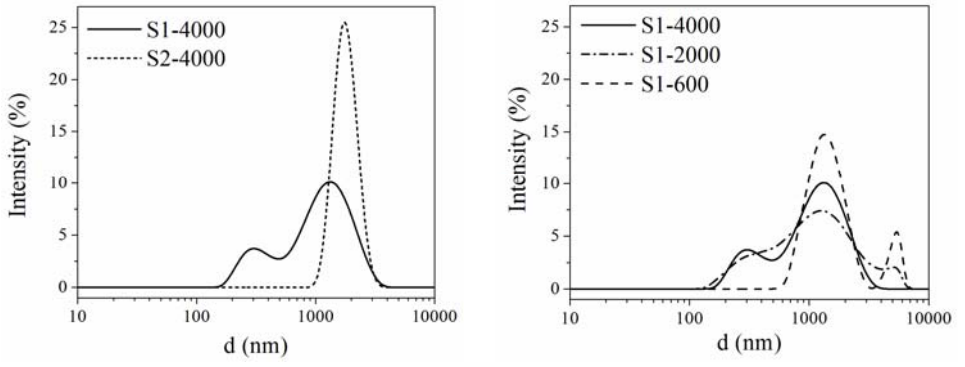

Figure 1. Particle size distribution of suspensions: (a) S1–PEG 4000 and S2–PEG 4000 and (b) S1–PEG 4000, S1–PEG 2000 and S1–PEG 600

It should be noted that all of the prepared suspensions have pale white color and that after the deposition of the coating onto the tile surface no visible change of tile color was noticed.

Surface roughness measurements

The average R_a values of the surface roughness measurements are given in Table 2. The deposition of coating slightly increases the surface roughness of the ceramic tiles. This increase is the smallest for the coating based on the PEG with the largest molecular mass. It can be again concluded that the use of PEG 4000 is favorable for the preparation of photocatalytic suspensions.

Table 2. Roughness properties of the coated tiles

Sample	R_a
Reference tile	2.236
C2–PEG 4000	2.304
C1–PEG 4000	2.642
C1–PEG 2000	2.768
C1–PEG 600	2.568

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Contact angle measurements

The results of the contact angle measurements are given in Table 3 and in Figure 2. The results show that all coated samples have higher values of the contact angles than the reference sample without coating. This indicates that the photocatalytic coating decreases the hydrophilicity of the ceramic tiles. Nevertheless, the contact angle on the coated samples decreases with the increase in the UV irradiation time (with the exception of sample C1–PEG 2000), showing the development of photo-induced hydrophilicity of the coatings.

Table 3. Contact angle values before UV/VIS irradiation and after 3.5 h of the UV/VIS irradiation

Sample	Before irradiation			After 3.5 h of irradiation		
	θc_i (°)	θc_r (°)	$\theta c_i - \theta c_r$ (°)	θc_i (°)	θc_r (°)	$\theta c_i - \theta c_r$ (°)
Reference tile	39.77	30.95	8.82	35.01	26.90	8.11
C2 – PEG 4000	93.99	77.29	16.70	87.29	71.81	15.48
C1 – PEG 4000	95.37	74.80	20.57	91.85	77.57	14.28
C1 – PEG 2000	98.60	79.88	18.72	102.68	87.00	15.68
C1 – PEG 600	88.98	70.22	18.76	86.11	67.23	18.88

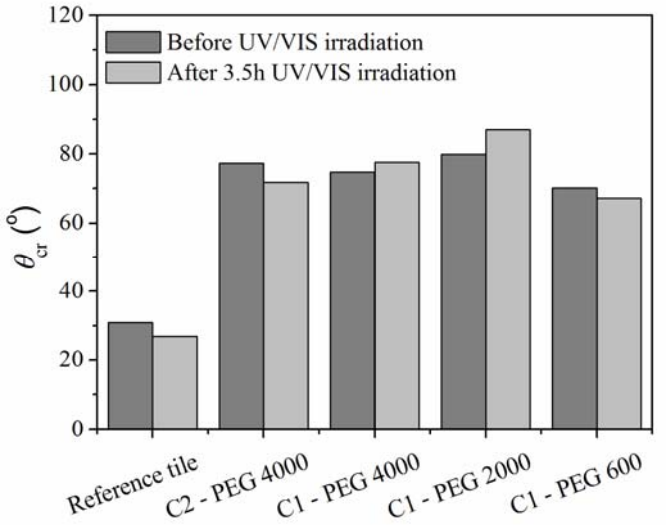

Figure 2. Average θc_r on the reference and coated tiles before and after 3.5 h of UV/VIS irradiation

Photocatalytic activity of coatings deposited on ceramic tiles

The efficiency of ceramic tiles with different photocatalytic coatings in the removal of Rhodamine B is presented in Figures 3 and 4. The comparison of the photocatalytic results of the coatings with PEG of different molecular mass and with different mass of the

photocatalyst in the case of PEG 4000 shows the following: (i) the coating prepared with the suspension having a larger amount of the photocatalyst, C2–PEG 4000, has the lowest photocatalytic activity among the studied series, justifying again the use of a smaller amount of the photocatalyst for the preparation of the coatings, (ii) the highest photocatalytic activity after 3.5 h of UV irradiation duration has the coating C1–PEG 2000 (28.16%), (iii) similar behavior has the coating C1–PEG 4000 with 1 mass% of the photocatalyst having the photocatalytic activity of 26.85% after 3.5 h of UV irradiation, (iv) the coating C1–PEG 600 with the lowest PEG molecular mass has the lowest activity among the studied series with different PEG. After 24 h of UV irradiation all studied coatings have similar and very high photocatalytic activity (about 80%). The results of the coating photocatalytic activity are in good agreement with the photo-induced hydrophilicity assessed by average contact angle of the water droplet. It can be concluded that coatings prepared from the suspensions with higher PEG molecular mass and smaller amount of the photocatalytic powder have a higher initial photocatalytic activity.

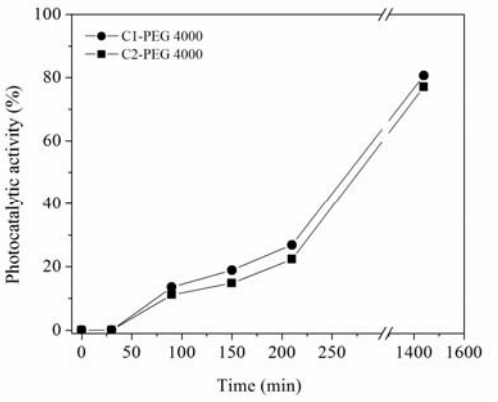

Figure 3. Photocatalytic activity of coated tiles with different amount of photocatalyst and PEG 4000

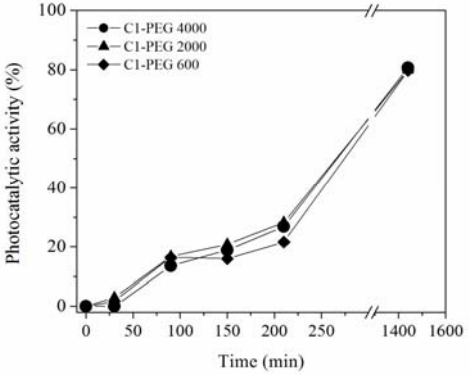

Figure 4. Photocatalytic activity of coated tiles with different PEG molecular mass

CONCLUSION

The study of the influence of the amount of photocatalytic powder in the suspension on the suspension particle size showed that the suspension with smaller amount of the photocatalyst (1 mas%) has better properties – smaller particle size. The results also showed that with the PEG of the highest investigated molecular mass (PEG 4000) is favorable for the preparation of the suspensions, since it gives the suspensions with preferable smaller particles. Nevertheless, all of the developed suspensions have particles that are microsized, which eliminates the health issues that occur in the case of usually used nanosized suspensions. The deposition of coating does not influence the roughness significantly. The coatings just slightly increase the surface roughness of the ceramic tiles, specifically in the case of the largest investigated molecular mass of PEG. The deposition of the photocatalytic coating decreases the hydrophilicity of the ceramic tiles. Nevertheless, the contact angle on the coated samples decreases with the increase in the UV irradiation time, showing the development of the photo-induced hydrophilicity of coatings. The results of the coating photocatalytic activity are in good agreement with the photo-induced hydrophilicity assessed by measuring the average contact angle. The coating prepared with the suspension having a larger amount of the photocatalyst has the lowest photocatalytic activity among the studied series, justifies the use of a smaller amount of the photocatalyst for the preparation of the coatings. After 24 h of UV irradiation, all of the studied coatings have similar and very high photocatalytic activity (about 80%). It can be concluded that the coatings prepared from the suspensions with higher PEG molecular mass and smaller amount of photocatalytic powder have higher initial photocatalytic activity. Generally, the use of PEG 4000 is favorable for the further investigation of the preparation of photocatalytic suspensions.

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КАРАКТЕРИЗАЦИЈА ФОТОКАТАЛИТИЧКИ АКТИВНЕ ПРЕВЛАКЕ НА БАЗИ TiO_2/Zn-Al ДВОСТРУКИХ СЛОЈЕВИТИХ ХИДРОКСИДА НА КЕРАМИЧКИМ ЦРЕПОВИМА

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Функција самочишћења (фотокаталитичка активност и површинска хидрофилност или хидрофобност) је за керамичке црепове од огромног значаја како са економског тако и еколошког становишта. Истраживање у овом раду је фокусирано на припрему одговарајућих фотокаталитичких суспензија проучавањем утицаја количине фотокатализатора и молекулске масе полиетилен гликола (ПЕГ) на особине самочишћења. Фотокаталитички материјал на бази Zn-Al двостуких слојевитих хидроксида са TiO_2 као фотокаталитички активном компонентом је синтетисан и употребљен за припрему фотокаталитичких суспензија. Керамички црепови са нанетом превлаком која у себи садржи мању количину фотокатализатора и највећу испитивану молекулску масу ПЕГ (ПЕГ – 4000) су показале највећу фотокаталитичку активност у реакцији разградње Родамина Б, као и одговарајуће површинске карактеристике.

Кључне речи: самочишћење, фото-индукована хидрофилност, површинске карактеристике, фотокаталитичка суспензија, TiO_2/Zn-Al двоструки слојевити хидроксиди

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