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Characterization of photocatalytic and superhydrophilic properties of mortars containing titanium dioxide

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ABSTRACT

Environmental pollution arising from industrial implants and urban factors is constantly increasing, causing aesthetical and durability concerns to urban structures exposed to the atmosphere. This work is aimed at the study of a system which could take advantage of functionalized building materials in order to improve the quality of urban surfaces, and possibly of the environment itself: TiO_2-containing photoactive materials represent an appealing way to create self-cleaning surfaces, thus limiting maintenance costs, and to promote the degradation of polluting agents. Several mortars containing anatase TiO_2, added as suspension or as powder, were characterized: among the photocatalytic mortars, the use of a combined additive (both powder and suspension) improved the material response. The best photoefficiency was exhibited by a mortar containing TiO_2 as surface covering; nevertheless, the adhesion problems shown by the surface layer open the way for future widening of investigations focused on the optimization of layer durability.

1. Introduction

Every year, an energy almost equal to 5×10^{24} J is provided by the sun and hits the surface of the Earth: this quantity is 10,000 higher than the real energy consumption per year of the whole world. The need to find a way to take advantage of this huge resource, together with the need for an improved quality of the environment, is driving architects and planners to combine the use of solar energy and functionalized building materials in order to limit the energy consumption and reduce pollution, specially concerning urban environments. The enormous surface area covered by building materials represents a useful way of exploiting solar energy, thanks to the noticeable technological improvements in energy and environment fields [1].

A new class of materials has been developed to meet these demands: photocatalytic materials, which are able to catalyze the mineralization of polluting agents, either organic and inorganic, through the presence of a semiconductor which produces strongly oxidizing and reducing species by means of the absorption of light energy [2–6].

Among the semiconductive materials, titanium dioxide (TiO_2) in the anatase form has proved to be the most interesting compound, thanks to its chemical stability, non-toxicity and reasonable price. In building industry, the use of TiO_2-containing materials [5] has allowed to obtain coating materials that combine the classical mechanical resistance and durability to a set of new properties, related to the improvement of the environmental conditions, since they promote the decomposition of polluting agents produced by exhaust emissions which adsorb on buildings' surfaces, and therefore the decrease of urban smog and fumes [7,8].

Besides the ecological concern, an aesthetic aspect is also involved. In fact buildings, monuments and any other infrastructure exposed to urban pollution will turn grey in time because of the adsorption of atmospheric particulates. A valid contribution to this topic can be found once more in TiO_2-containing materials since they allow an easier maintenance of the original color of the surfaces thanks to the superhydrophilic properties of the manufact, which consist in the generation of a hydroxylated surface layer that improves surface wettability, and therefore its cleaning properties [9,10]. These materials are therefore defined as self-cleaning, and their use in building industry can grant a reduction of maintenance charges [11].

The present work deals with the study of the surface properties of photocatalytic manufacts obtained by adding anatase to the mortar that constitutes the external layer of the manufact. This evaluation has been carried out by examining both the photodegradation of organic compounds and the onset of the superhydrophilic behavior, in terms of variation of contact angle of water on the surface and self-cleaning attitude.

The tested materials consist of white mortars: the presence of pigments and their interaction with the photoactive component, which is not considered in this research, will be analyzed in future work.

2. Methods

Tested materials were fiber-reinforced mortars containing anatase, which was added to the mix design in different percentages either in

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Table 1
Tested samples: anatase percentage content (TiO_2 versus cement weight)

Code	TiO_2 powder (%)	TiO_2 suspension (%)	Total TiO_2 content (%)
A	_	_	_
B	_	2	2
C	1	1	2
D	_	3	3
E	1	2	3
F	2	1	3
G	_	5	5
H	2.5	2.5	5
I	3	2	5
J	5	_	5
K	_	10	10
L	_	As surface covering	As surface covering

the form of nanometric powder, or as aqueous suspension, or as surface covering (Table 1). Typical diameter of TiO_2 particles were 88 nm for TiO_2 suspension, which had a pH value of approximately 6 (commercial suspension purchased by Degussa), while TiO_2 powder had a particle size ranging from 150 to 400 nm (commercial powders purchased by Precheza), having purity higher than 92%; data were supplied by manufacturers. The different particles characteristics are expected to give rise to different photocatalytic efficiencies [3,4]. In the case of bulk addition anatase was added in the percentage specified in Table 1; the surface covering was obtained by spreading the aqueous suspension on the surface of the manufact after drying, therefore an assessment of its percentage is difficult.

All tests were performed both on anatase-containing samples and on a mortar which didn't contain any photoactive component, being the latter considered as reference. All mortars were characterized by the same mixture proportion, exception made for the anatase content: in particular, no pigments were added to the mixture and the chosen water–cement ratio was 0.56 (Table 2). Samples were cut into two different geometries depending on the test method: square samples 50 mm × 50 mm and round samples with diameter 25 mm, both 8 mm thick.

Samples photocatalytic activity was characterized in the mineralization of Volatile Organic Compounds (VOC): in particular, 2-propanol was chosen as model reactant of organic compounds present in the atmosphere [12]; only round samples were used. The source of UV light was an Osram Vitalux lamp (300 W). In these tests, as well as in further tests involving UV light, the UV intensity was 2 mW/cm^2.

Samples were put in a quartz cell, whose atmosphere was saturated with 2-propanol by forcing air to flow inside a flask containing the organic compound and subsequently inside the reaction cell (Fig. 1). The cell was supplied with a seal plug that allowed to take air samples from the cell, which were analyzed with a gas chromatograph (GC) in order to evaluate the 2-propanol quantity inside the cell and its variation in time.

After allowing the air flow for 10 min the cell was closed and a first GC analysis was performed on a 30 μL sample of the inner atmosphere; then the cell was irradiated with UV light for a total time of 23 h. During this time, two GC analyses were performed, after 3 h and 6 h of UV exposure; a final analysis was performed at the end of the test.

Table 2
Mortars mixture proportion, exception made for TiO_2 content (percentages are considered with respect to cement weight)

Portland cement (CEM I 42.5 R)	555 kg/m^3	
Silica sand	1110 kg/m^3	
W/C ratio	0.56	
Expansive admixture	33 kg/m^3	6%
Waterproof additive	22 kg/m^3	4%
Glass fibers	20 kg/m^3	3.6%
Antifoaming admixture	1 kg/m^3	0.1%

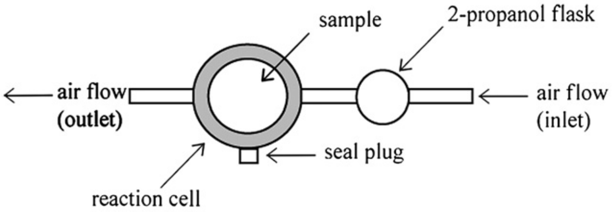

Fig. 1. Reaction cell scheme for 2-propanol mineralization (top view).

2-propanol is photodecomposed to acetone and water: the chemical reaction is given in Eq. (1).

$$CH_3-CH(OH)-CH_3 \xrightarrow{UV,\ TiO_2} CH_3-CO-CH_3+H_2O \tag{1}$$

GC analyses allowed monitoring the quantity of both 2-propanol and its reaction product, acetone, present in the inner atmosphere of the cell: in this way, it was proved that 2-propanol concentration decreased due to its mineralization. Acetone percentage inside the cell with respect to 2-propanol was calculated from GC peaks as follows (Eq. (2)):

$$\%\text{acetone} = \frac{[\text{acetone}]}{[\text{acetone}]+[\text{2propanol}]} \times 100 \tag{2}$$

being [acetone] and [2propanol] the moles of the two organic compounds revealed by GC in the 30 μL of atmosphere subtracted from the cell for the analysis.

The square samples were used in atmospheric exposure tests. Samples were put on a tilted net (45° with respect to the ground), which avoided stagnating rain water on samples surfaces. The net was then placed on the roof of a building (approximately 15 m altitude) and therefore exposed to the polluted urban atmosphere of Milan, facing South in order to maximize the exposure to sunlight. Thus, during exposure samples could benefit of both solar light, which is able to activate the photoinduced phenomena, and rain, which provided the water necessary for the self-cleaning process to establish. Samples were white at the beginning of the test, but after some time they showed a tendency to turn grey, due to powders and polluting agents adsorption on their surfaces: therefore, color was monitored as indicative parameter of the photoactivated self-cleaning attitude of samples. Color measurements were performed with a spectrophotometer CM-2600d (Minolta), which gives the chromatic coordinates of the measured color in terms of the color space L^*, a^*, b^* defined by CIE (Commission Internationale de l'Éclairage); the color variation in time (ΔE) can be measured as spatial difference between two points, corresponding respectively to the color at the time t and to the initial color at $t=0$ (Eq. (3)) [13,14].

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \tag{3}$$

being $\Delta L^* = L_t^* - L_0^*$, $\Delta a^* = a_t^* - a_0^*$, $\Delta b^* = b_t^* - b_0^*$.

Finally, the materials wettability was studied through contact angle measurements. First, a water drop with a volume of 10 μL was placed on the sample surface with a precision pipette: the drop image was acquired through a CCD camera and then elaborated with an image analysis software, which allowed a precise measurement of the contact angle between water and the tested mortar (Fig. 2). Subsequently the mortar was irradiated with UV light for different periods of time, after which the contact angle measurement was repeated.

3. Results and discussion

3.1. VOC degradation

2-propanol mineralization tests evidenced the particularly intense photoefficiency of some of the tested samples after 6 and 23 h

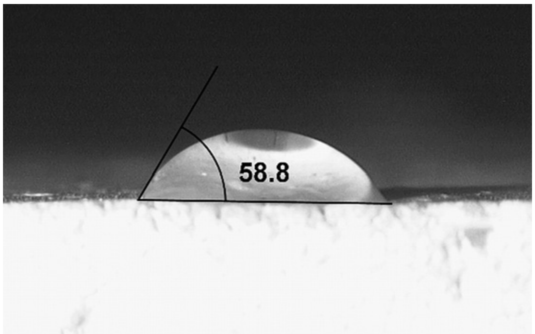

Fig. 2. Measurement of contact angle of water on samples surface with image analysis software.

irradiation (Fig. 3). Results are shown in terms of acetone formation inside the cell with respect to quantity of 2-propanol present in the cell atmosphere, see Eq. (2). First, it is important to notice that 2-propanol is slowly decomposed by the bare action of UV light: tests performed on sample A, which didn't contain any TiO_2, led to the formation of a very small quantity of acetone (approximately 1% after 6 h and 2.5% after 23 h). In fact, while anatase can sometimes promote reactions which do not happen under normal irradiation conditions without the presence of semiconductive species, its primary role is to catalyze, and therefore accelerate, reactions thermodynamically allowed but which show extremely slow kinetics.

As expected, the degradation extent was proved to increase with irradiation time, as well as with anatase content, up to an anatase content of 10% in the bulk material (sample K), which was the maximum percentage tested: in fact, higher contents of anatase would have led to a decreased mechanical resistance of the manufacts.

The highest 2-propanol conversion percentage after 23 h of UV exposure are obtained in the case of the sample covered with a photocatalytic layer (sample L). In this case, the whole quantity of photoactive component is concentrated on the material surface and no anatase is present in the bulk of the mortar: therefore, an optimal utilization of the photocatalytic species is reached, since all anatase is on the surface, and therefore available to activate photocatalytic processes.

Good efficiencies, with an acetone production higher than 30%, were also noticed for samples H and I, which contained 5% of anatase as a mixture of nanometric powder and aqueous suspension.

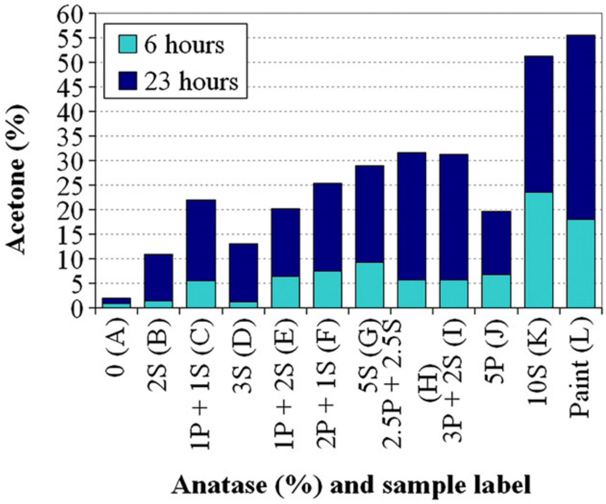

Fig. 3. Acetone formed after 6 h and 23 h of exposure to UV light as the reaction product of the photodecomposition of 2-propanol in presence of the tested materials (P = powder, S = suspension).

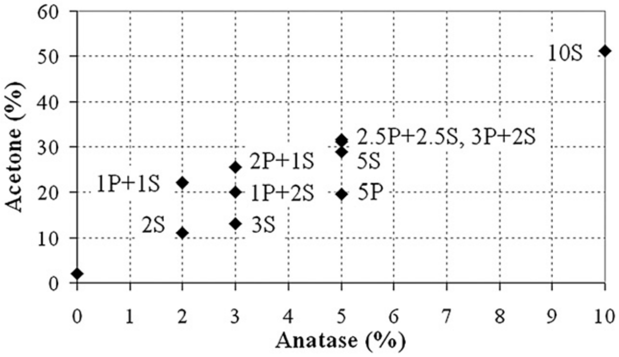

Fig. 4. Acetone formed after 23 h exposure to UV light as a function of anatase percentage and type of admixture (P = powder, S = suspension).

An interesting behavior was observed for samples containing the same TiO_2 amount, but in different forms, which in turn means with particle size of two different orders of magnitude (Fig. 4). A first example is represented by samples D, E and F, which contain 3% of anatase, added in the first case as aqueous suspension (low dimension particles) and in the other two samples as a mixture of powder (high dimension particles) and suspension. The latter type of addition proves to be more efficient, giving rise to a synergic effect: in fact, while sample D promotes the degradation of about 13% of the 2-propanol contained in the cell, the other samples grant a conversion higher than 20%. The same behavior can be noticed for samples G, H, I and J, all containing 5% of anatase, whose mineralization percentages are 29%, 32%, 31% and 20%, respectively: it is clear that the aqueous suspension confers to the material a higher photoactivity with respect to the tested anatase powder, and this is evidently due to the particle size, being the particles in suspension almost one order of magnitude smaller than in powder. Once more, the mixture of the two species enhances the photocatalytic efficiency.

3.2. Atmospheric exposure

These tests evidenced the self-cleaning attitude of the analyzed mortars, under in-field experimental conditions which lasted approximately 4 months; during this time samples experienced two different periods: in a first period, which lasted 70 days, they were exposed to urban environment, while for the resting 50 days they were kept inside a chamber provided with lamps whose irradiance spectra simulated the solar spectrum. The latter period was formulated in order to understand whether an artificial irradiance reproducing sunlight could really promote a self-cleaning process, splitting this contribution to color variation from the interfering aspect of the continuous adsorption of species on the surface (Fig. 5).

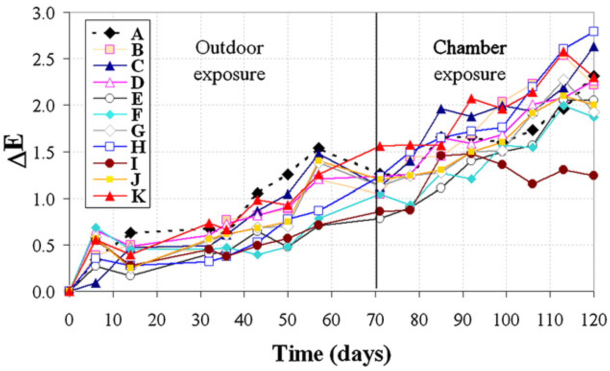

Fig. 5. Color variation experienced by the tested materials, first exposed to a polluted urban environment and after 70 days collocated in a closed chamber.

A first observation should concern the behavior of the photoactive mortars with respect to the reference mortar, prepared without any TiO_2 addition: some of the tested materials didn't show any photoactivated phenomena, since their final color variation was equal to, or higher than, the color variation observed for the reference mortar ($\Delta E=2.3$). On the other hand, in one case the self-cleaning properties were undoubtedly activated by solar light: in fact, on sample I the color variation was limited to a ΔE value of 1.2. Among the tested materials, the worst behavior was presented by sample L, which was the most performing material in photocatalytic experiments. This sample didn't contain any anatase in bulk: the photoactive component was present in a surface layer deposited as a paint on the material surface. Its poor self-cleaning behavior was due to the partial detachment of the surface layer under environmental conditions, that is, wind and rain: therefore, measurements relative to this sample are not shown in Figs. 5–7 since the coating detachment doesn't allow a reasonable comparison with the color variation noticed for the other samples. From these considerations it can be stated that this type of material cannot be recommended for outdoor applications, though it showed the best photocatalytic performances.

Another observation can be made on the self-cleaning attitude in outdoor exposure: samples activity doesn't respect the efficiency classification that could be inferred from photocatalytic tests, and samples having same anatase percentage showed different behavior. This is due to the fact that this phenomenon is made of two components: the photocatalytic activity (degradation of pollutants adsorbed on the surface) and the superhydrophilicity establishment (which allows the surface to be more easily cleaned by rain). The response of different materials to these two activation processes can be different: therefore, though e.g. samples G and H both contain 5% of anatase, their behavior is controlled by the type of addition (powder versus suspension, with different granulometry and different interaction with the cementitious matrix) rather than by the nominal composition. This issue must be considered in the evaluation of self-cleaning attitude of a material, since the determination of this property is the most promising and interesting for real industrial applications.

An interesting behavior arises from the analysis of the two different exposure periods, that is, outdoor and inside the chamber. In the former case almost all samples underwent a color variation comparable, or even inferior, to that of the reference sample; on the contrary, in the second period samples C and H showed an increased rate of color variation. This behavior can be interpreted by looking at the trends shown by the single chromatic coordinates (Figs. 6, 7). In particular, only ΔL^* and Δb^* data will be presented, since Δa^* values are irrelevant: in fact, Δa^* ranges from 0.12 to 0.35, while ΔL^* and Δb^* range from −0.75 to −2.25 and from 1.22 to 1.85, respectively; moreover, from CIE standards the minimum color variation which can be noticed by human eye is considered to be 0.5 for grayscales and 1 for colors [14].

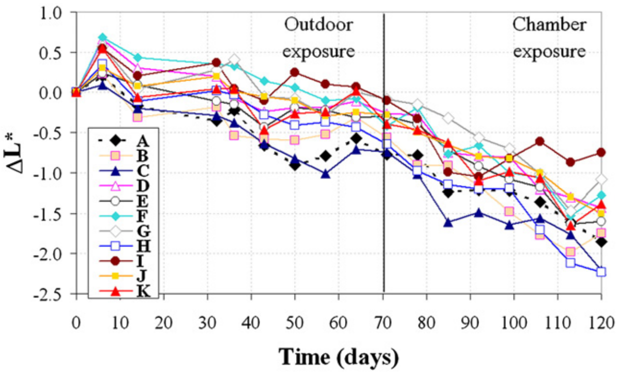

Fig. 6. Brightness variation (from white to grey) experienced by the tested materials.

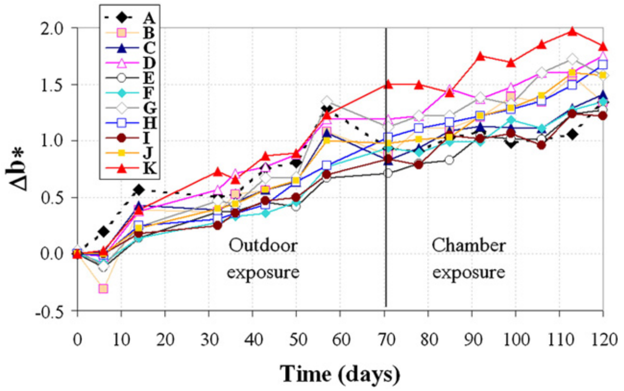

Fig. 7. Variation of chromatic coordinate *b** (from blue to yellow) experienced by the tested materials. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

From changes in the coordinate b^*, ranging from blue to yellow, a shift towards a slightly yellow hue can be noticed. This shift was more evident for samples which showed a higher photocatalytic activity and was partially recovered in time, thus suggesting that its cause could be the mineralization of organic compounds formerly adsorbed on the surface.

Nevertheless, the color variation after the interruption of the atmospheric exposure was non-negligible both for b^* and L^*, thus showing a low photoactivity. This is ascribed to the absence of water, which is of fundamental importance for the self-cleaning process: in fact, during the first period of exposure to environment samples surfaces could benefit from rain water, and therefore self-cleaning could be accomplished, while in the second period only the photocatalytic degradation could be achieved.

3.3. Hydrophilic properties

Contact angle formed by water on samples surface was measured in order to assess how samples wettability changed after UV irradiation. These tests were intended to evaluate if it was possible to reach a state of superhydrophilicity, ascribable to the photoactivity of the surface.

Fig. 8 shows the percentage variation of contact angle, referred to its initial value (on average, 50°), after 4 days of exposure to UV light. For each sample, contact angles both before and after irradiation were calculated as an average over at least 4 drops of water put on the surface. In fact, the samples surface was quite irregular: this method was meant to take into account the behavior of the whole surface and minimize variations due to irregularities on the surface. Only 4 drops

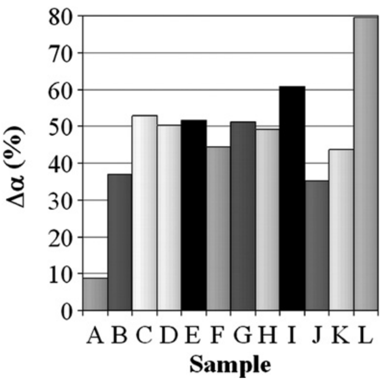

Fig. 8. Percent decrease of contact angle of water on the tested materials after 4 days of UV exposure with respect to values measured before UV irradiation.

were analyzed since it was noticed that data dispersion was acceptable.

Some samples show a remarkable decrease of contact angle value: anyway, once more the best results were obtained with samples H and L, which show as expected the highest photoactivity. Sample K, which contained the higher percentage of anatase, didn't show a particularly high decrease of contact angle values after irradiation: nevertheless, it must be noticed that the starting contact angle of this sample was already lower than that of the other samples (this was the only exception), therefore the final contact angle was comparable to that of sample I, thus demonstrating the establishing of superhydrophilicity. The excellent photoactivity of sample L had already been noticed in photocatalytic tests; nevertheless, this type of photoactive mortar cannot be considered for commercial applications due to its big adhesion drawbacks, which require further studies fully dedicated to the production processes of this mortar and to the application of the photocatalytic covering. The unsuitability of mortar K, on the other hand, is due to commercial reasons: the high anatase percentage would in fact require a high rise in mortar prices.

4. Conclusions

In this work, 11 different mortars with same mixture proportion, exception made for the anatase content, were characterized: as expected, all mortars containing TiO_2 were proven to show photocatalytic properties. Nevertheless, the final aim of the research was to set up a mortar composition with optimal photoactivity, but at the same time commercially attractive: therefore a too high anatase content, which would undoubtedly lead to a performing product, cannot be taken into account since it would cause an excessive increase of the production costs.

A good compromise between photoactivated properties and anatase content was found to be the sample containing 3% of anatase powder and 2% of anatase suspension; in fact, it was noticed that a mixture of the two different forms of anatase led to synergic effects with respect to mortars with equal content of anatase added only as powder or as suspension. The mentioned sample allowed achieving both a good conversion in photocatalytic tests and a noticeable variation of the interaction of water with the surface, which became superhydrophilic after UV irradiation. These two properties led to a pronounced self-cleaning attitude. Much effort will be dedicated in future research to the development of photoactive surface coverings with improved adhesion properties to ensure better durability.

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