HUMIDITY AND TEMPERATURE INFLUENCE ON THE SELF-CLEANING PERFORMANCE OF BUILDING MATERIALS CONTAINING THE PHOTOCATALYSTS

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Abstract

Titanium dioxide is a well-known substance for its photocatalytic properties. The aim of this article is to describe the influence of humidity and temperature on the self-cleaning properties of construction surfaces covered with a layer of titanium dioxide (further labeled as TiO_2). Its bandgap allows for the use of its photocatalytic properties strictly when exposed to the UV irradiation. The physico-chemical characteristics of the used TiO_2 were investigated and described using analytical methods: x-ray diffraction spectroscopy (XRD), diffuse reflectance spectroscopy (DRS) and scanning electron microscopy (SEM). The experiments carried out aimed to identify the effect of humidity and temperature on the self-cleaning performance of TiO_2 coated surfaces. The effect of humidity was tested at 20, 40, 60 and 80 % of relative humidity in testing chambre, the temperature was kept constant at 20 °C. The effect of temperature was tested for the 10, 20 and 30 °C, and the relative humidity was kept constant at 60 %. It was observed that increasing of relative humidity always led to higher self-cleaning performance. With respect to the temperature effect, a more complicated relationship was observed between the temperature and self-cleaning performance. The lowest self-cleaning ability was observed for the samples tested at 20 °C. The highest self-cleaning effect was observed for samples tested at 10 °C; this effect was slightly lower for samples tested at 30 °C. The best self-cleaning performance was observed for the experimental conditions of 80% RH and 10°C. Relative humidity was identified as a key factor influencing the self-cleaning ability of TiO_2 coated cement pastes.

Keywords: Photocatalysis, titanium dioxide, cement pastes, self-cleaning properties

1. INTRODUCTION

Nowadays, TiO_2 is the most studied substance among all photocatalysts [1]. Its accessibility and chemical stability provide humanity with a wide range of application of TiO_2 in nanotechnology [2], medicine [3], wastewater treatment [4]. and manufacturing industries [5]. Over the last 30 years, the construction industry has also begun to show its interest in photocatalysts application in building materials. ISO UNI 22197:2007 and UNI 11247:2007 standards [6,7] were developed specially for the testing of the photodegradation properties of TiO_2 if used in building materials. Since a suitable form of TiO_2 is one of the most accessible photocatalysts that also show a self-cleaning effect, TiO_2 has quickly started to be used as a cement additive or building surface coating, which also reduces construction maintenance costs [8].

The most stable TiO_2 phase modifications are anatase and rutile with band gaps of 3.2 eV and 3.02 eV [1,5]. These energies correspond with wavelengths at 385 and 410 nm of light radiation, which means that pure photocatalytically active TiO_2 shows its self-cleaning capabilities exclusively when exposed to the UV irradiation without being doped with other additives [9]. Nevertheless, if solar light may provide enough UV radiation, photocatalysts still require water as a necessary resource for the photodegradation process. In that case, active centers of TiO_2 use humidity contained in the surrounding atmosphere to produce hydroxyl $\cdot OH$ and superoxide $\cdot O^2$ radicals, which are well-known for their high oxidizing properties [10]. It was figured out, that during different periods of a year, photocatalytic coatings show different photodegradation activities as well [11]. In our work, we focused on the study of the effect of relative humidity and temperature on the self-cleaning ability of surfaces coated with photocatalytically active TiO_2.

2. MATERIALS AND METHODS

2.1 Sample preparation

TiO_2 photocatalyst used for the experimental part is an AEROXIDE® P25 (further labeled as P25), containing its two crystal phases - anatase and rutile. In the first step, the suspension of P25 with exact concentration of 4 $g \cdot dm^{-3}$ was prepared. In order to eliminate inaccuracies during application process, the suspension was properly homogenized with ultrasonicator OmniSonic Ruptor 400.

In the second step, samples of cement pastes were prepared. In sum, 3 samples of cement paste (one reference sample, and two samples for coating with TiO_2) were prepared for testing at selected temperature and humidity. The cement paste was made with 150 g of cement (CEM I 42,5R) and 55 ml of water, the resulting mixture was then poured into three equal steel forms (100 x 50 x 10 mm) and put into the humidity box. After the 24 hours of hardening, fresh hardened samples were unmold and stored in a moist environment for one week. After that period, the samples were let to dry 24 hours in laboratory conditions with aim to eliminate the surface moisture as it can undesirably affect the application process of P25 suspension on the surface of pastes.

In the last step, the P25 suspension was evenly applied on the surface of samples with a lab sprayer. The surface of each sample was coated with three approximately equal layers, applied one by one after the previous one completely dries. Such prepared samples were stored in a dark at laboratory conditions for 24 hours before the initiation of self-cleaning test. The rest of the suspension volume prepared was not used.

2.2 Characterization methods

X-ray diffractometer Miniflex600 (Rigaku, Japan) was used for registration of diffraction patterns of P25. An X-ray lamp, which has a cobalt anode, was operated at 40 kV and 15 mA. Primary optics included a 2.5° divergence Soller aperture and a 1.25° divergence aperture. Secondary optics included a 2.5° Soller aperture and a K_β filter made of iron foil. D/tex Ultra 250 operated in 1D mode was used as a detector. The measurement was performed in the range of 10-100 °2 theta, with a step of 0.2 ° and at a speed of 3 °/min.

Scanning electron microscope Aspex Explorer (Thermofisher Scientific, USA) was used for SEM analysis of the surface of P25 particles. Cerium hexaboride used as a thermoemission source of electrons in this microscope operated at an accelerating voltage of 15 keV. Secondary and backscattered electrons were detected using SE and BSD detectors, the chemical composition was studied using an energy dispersive detector (EDS).

UV-VIS Diffuse reflectance spectroscopy was performed on spectrometer UV-2600 (Shimadzu, Japan). The instrument in the DRS configuration is equipped with an IRS-2600Plus integrating sphere. Registration of DRS spectra was performed in the range of 220 - 800 nm. The indirect bandgap energy of P25 sample was evaluated with Tauc's plot.

The self-cleaning test was conducted by the discoloration of rhodamine B applied on the surface of TiO_2 coated cement pastes. The modified procedure, based on standard UNI 11259, was used for this purpose. Our procedure included application of rhodamine B solution with concentration of 50 $g \cdot dm^{-3}$ on the sample surfaces using lab sprayer. The amount of RhB on each sample was calculated gravimetrically giving approximately 80 mg of P25 deposited on the surface of each sample. Such prepared samples were left 24 hours in Memmert ICH110 L climate chamber at conditions defined for given test (temperature and relative humidity). After this period, the own self-cleaning test was initiated by switching-on the UV light and lasted for 26 hours. To monitor the discoloration process (RhB degradation), L*a*b* coordinates were measured with MiniScan EZ spectrometer (HunterLab, USA) at the 0 h (before the irradiation was initiated), 4 h, and 26 h of 26 h of irradiation. Self-cleaning performance of TiO_2 coating at given combination of temperature and relative humidity was determined based on the change of the a* coordinate in a given time period (4, and 26 h) relative to its original value obtained before the irradiation was started (0 h).

3. RESULTS AND DISCUSSION

3.1 Characterization of P25

X-ray diffraction pattern of P25 photocatalyst is shown in **Figure 1** and confirms the presence of two TiO_2 modifications, anatase and rutile, respectively.

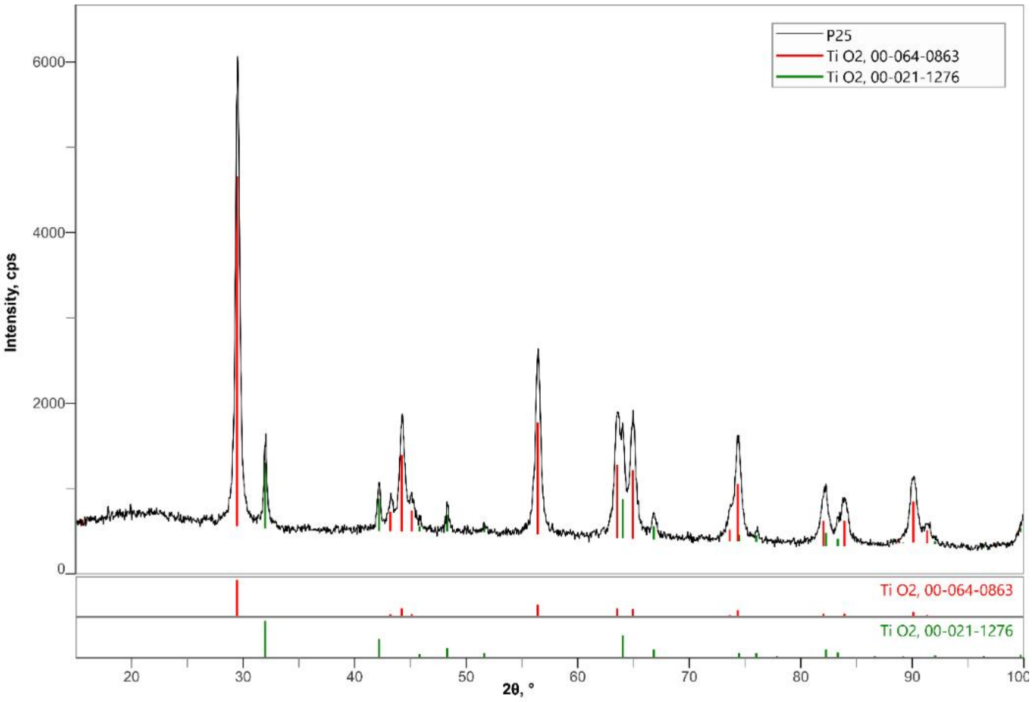

Figure 1 X-ray diffraction analysis of P25

Figure 2 describes the DRS spectrum of the P25 sample. **Figure 3** describes the Tauc's plot [12]. It was used to evaluate the optical bandgap of this sample, and the value of 3.3 eV was achieved. This value is closely similar to the value 3.2 eV typically reported for anatase and reflects the dominant contribution of anatase phase to Eg values. It should be noted that a slightly higher value of Eg than 3.2 eV was observed also by other researchers, for example, by Feng et al. [13].

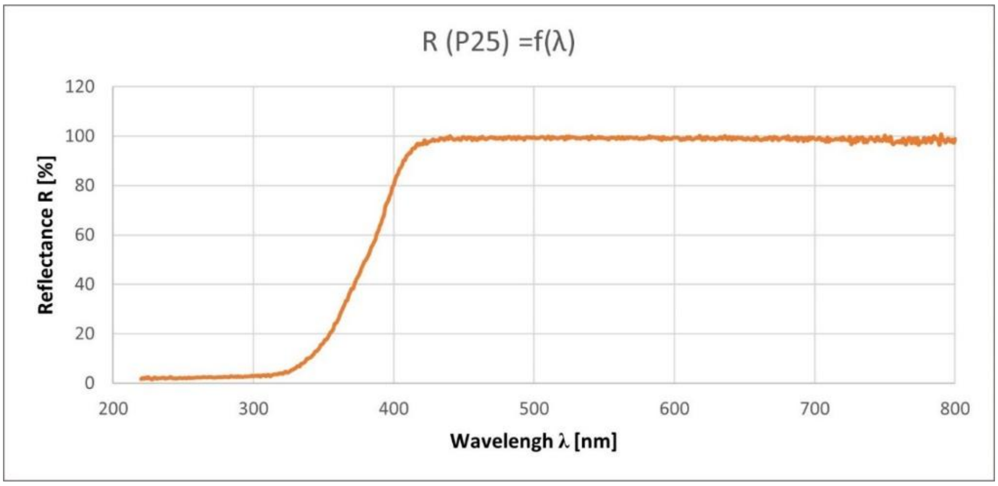

Figure 2 DRS spectra of P25 sample

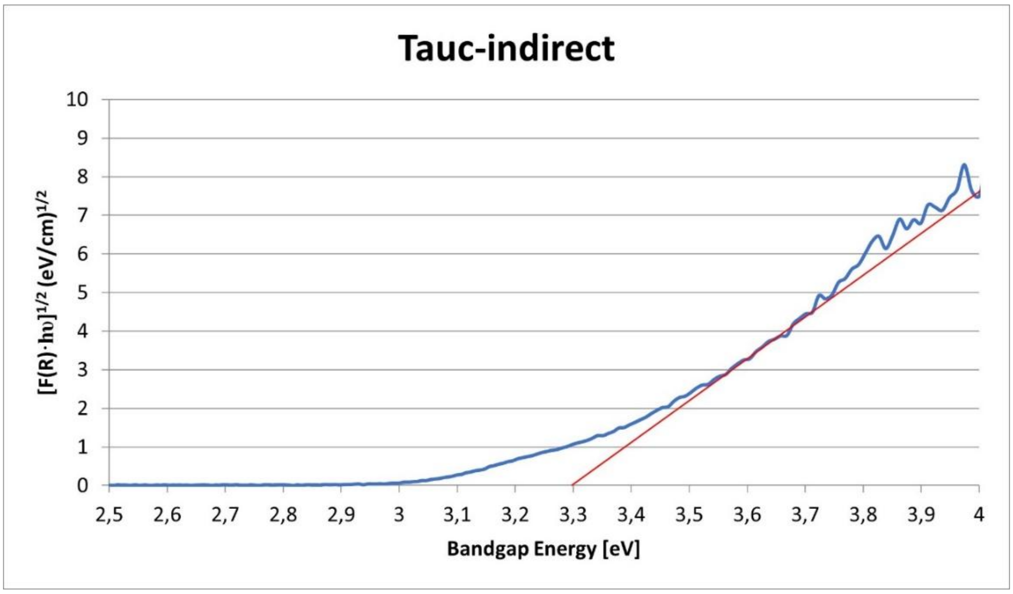

Figure 3 Tauc's indirect plot

Figure 4 shows the morphology of P25 observed with SEM technique and it is evident, that the individual TiO_2 nanoparticles form larger aggregates.

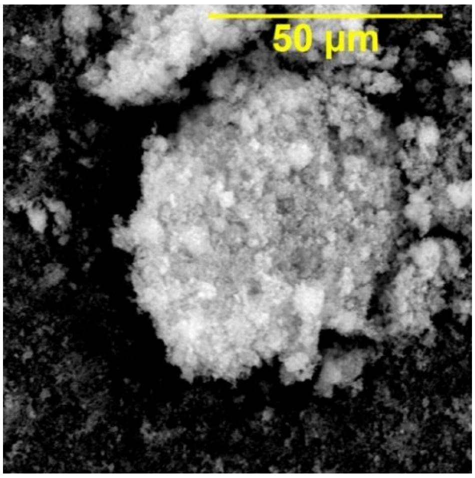

Figure 4 SEM image of P25 particle

3.2 Testing of the effect of humidity and temperature on self-cleaning performance

Figure 5 demonstrates the influence of humidity on the self-cleaning performance of TiO_2 coated cement pastes, while the temperature remained constant at 20 °C during all experiments. As can be seen, increasing the relative humidity led to an increase in the self-cleaning performance. Higher relative humidity is associated with a higher number of water molecules in the testing chambre. The self-cleaning performance of the surfaces of the samples is based on the photodegradation activity of TiO_2, which is related to the formation of hydroxyl and superoxide radicals from H_2O molecules. In general, the higher the humidity is, the higher the number of water molecules are available for the formation of hydroxyl and superoxide radicals. **Figure 5** shows that there is a linear relationship between photodegradation activity and humidity.

Figure 6 shows the impact of temperature on self-cleaning performance at 60% of relative humidity. The temperature relationship of self-cleaning performance is more complicated than was observed in the case of the relative humidity. The highest self-cleaning performance was observed at a temperature of 10 °C, while the minimum performance was observed for a temperature of 20 °C. This relation is attributed to the fact that with the growing temperature the number of water molecules absorbed on the surface is decreased because of their larger evaporation. On the other hand, a higher self-cleaning performance registered at 30 °C can be connected with the effect of temperature on the RhB degradation kinetics.

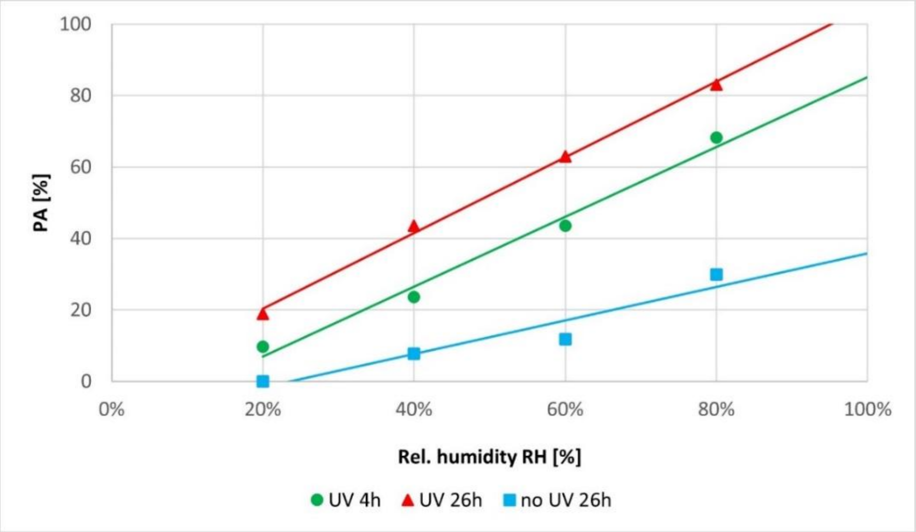

Figure 5 Relative humidity impact on photodegradation activity at 20 °C

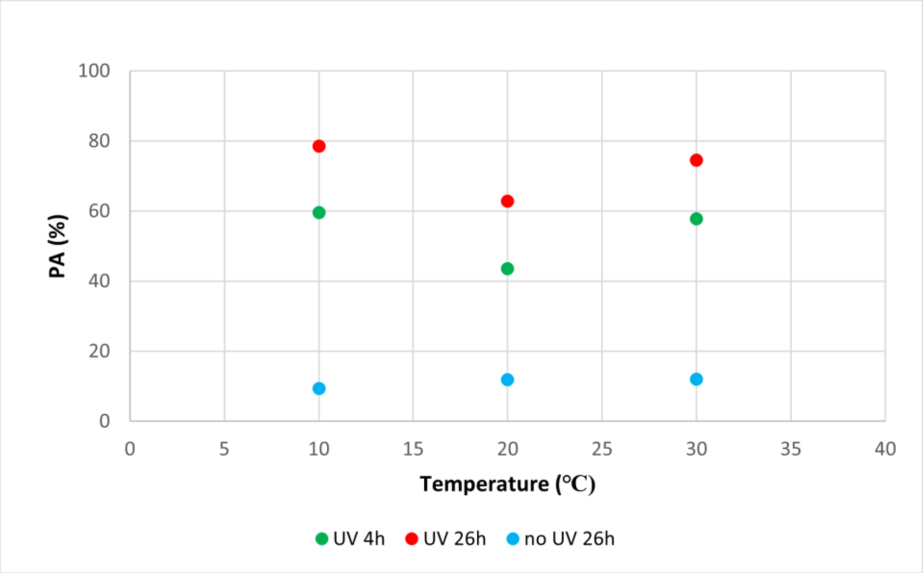

Figure 6 Temperature impact on self-cleaning performance

4. CONCLUSION

This work was devoted to studying the influence of relative humidity and temperature on self-cleaning capabilities of building materials coated with TiO_2 as photocatalyst. In the case of humidity, the positive effect of its increasing value was observed and explained by higher amount/number of water molecules present on the tested surface. It was observed that the dependence of the self-cleaning performance on humidity has linear character.

The second important finding is the effect of temperature on the self-cleaning ability of the samples. The test was carried out at temperatures of 10, 20 and 30 °C and a constant relative humidity 60 %. The decolorization of the tested surfaces caused by the photodegradation of RhB dye was the least effective at a temperature of 20 °C, while the most effective was at 10 °C. This effect could be attributed to the fact that the lower temperature leads to the condensation of a higher number of water molecules (larger volume of water vapor) and higher retention of condensed molecules on the surface. The water molecules retained on the surface of the TiO_2 coating can produce hydroxyl and superoxide radicals after irradiation with light of a suitable wavelength. A higher number of originated radicals caused a higher extent of RhB degradation and thus a higher level of surface discoloration. Increasing the temperature to 30 °C resulted in an increase in the self-cleaning ability of the surfaces of cement pastes compared to the experiment at 20°C, which can generally be explained by the positive effect of the higher temperature on the rate of chemical reactions.

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DATA AVAILABILITY

10.5281/zenodo.13918261

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