# Evaluation of the Best Solution for the Functionalization of Photocatalytic, Superhydrophobic, and Self-Cleaning Properties on Asphalt Mixtures

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**Abstract.** This research aims to develop asphalt mixtures with new capabilities with photocatalytic, superhydrophobic, and self-cleaning capabilities. Different solutions were prepared combining nano-TiO<sub>2</sub> and micro-PTFE on water, and ethyl alcohol and dimethyl ketone with different concentrations. The solutions were sprayed over the asphalt mixtures and the new capabilities were evaluated via decolourization of Rhodamine B dye aqueous solution under simulated solar irradiation and Water Contact Angle measurements. Among the combinations analysed, the best solution was TiO<sub>2</sub> PTFE with ethyl alcohol (8 g/L).

## **1** Introduction

The coatings composed of nano/microparticles applied over asphalt mixtures provide new capabilities (i.e., functionalization) such as: photocatalytic, to photodegrade pollutants for the purpose of air cleaning; superhydrophobic, to improve road safety; and selfcleaning, to avoid slipping problems [1,2].

Road pavements are ideal infrastructures to reduce air pollution levels due to their enormous surface area, as well as their proximity to the pollutant gases (mostly from vehicles), especially in urban areas [3]. When functionalized with semiconductor materials, the photocatalytic process on roads is initiated by the electron's excitation from the valence band to the conduction band via photons with proper energy. Then, charge carriers are formed (electrons  $e^{-}$  and holes  $h^{+}$ ). They can react with oxygen and humidity, generating free radicals which can degrade, for example, NO<sub>x</sub>. This functionalization also endows the material self-cleaning properties, which are related to the degradation of organic compounds, such as oils and greases. This effect can mitigate the decrease of friction caused by the contamination of the road surface by these pollutants [4].

The benefits of providing superhydrophobic capability to asphalt mixtures are mainly to increase water repellency and prevent ice formation. Therefore, the decrease of friction caused by the presence of water / ice over the road surface can be reduced. In this specific case, the self-cleaning effect is based on water droplets' ability to carry dirt particles.

First, different types of solutions were prepared with nano-TiO<sub>2</sub> (titanium dioxide) and micro-PTFE (polytetrafluoroethylene) with water, ethyl alcohol and dimethyl ketone using different concentrations (4 and 8 g/L). It was not possible to prepare aqueous solutions with PTFE since the particles cannot be dispersed into this medium. The method of application of the particles was by spraying solutions over the surface of a conventional asphalt mixture already compacted. The solutions were sprayed over the asphalt mixture samples (8 mL/cm<sup>2</sup> at room temperature) with the dimensions of 25×25×15 mm<sup>3</sup> in order to choose the best solution. The (functionalized) asphalt mixture samples were named by an alphanumeric string, which starts by AC 10 to indicate the asphalt concrete, the particle used (TiO<sub>2</sub> and/or PTFE) and then the solvent used (W - water, ETH - ethyl alcohol, and CET - dimethyl ketone), respectively. If both particles, nano-TiO2 and micro-PTFE, were combined, at the end of the string, the concentration of the solution was inserted, for example, AC 10 TiO2PTFE-ETH-8g/L. In this case, 4 g/L and 8 g/L represent 2 g/L and 4 g/L of each solute, respectively. In case of the solutions with just one type of particles, the concentration was 4 g/L.

The photocatalytic efficiency was evaluated via Rhodamine B (RhB) degradation following [5,6]. The (functionalized) asphalt mixture samples were immersed into 30 mL of RhB aqueous solution with a concentration

<sup>2</sup> Materials and Methods

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of 5 ppm. The systems were placed inside a box containing a light, located 25 cm above them, that simulates the sun irradiation (power intensity of  $11 \text{ W/m}^2$ ). After 3 h in dark condition, the samples were irradiated during 8 h. In this way the adsorption and photocatalysis could be split and the photocatalytic efficiency analysed. To avoid the evaporation of RhB solution, and consequently the concentration increase, all the systems were closed with a transparent plastic film with at least 90% of transmittance (between 292 and 900 nm). The maximum absorption (554 nm<sup>-1</sup>) of the dye was evaluated as function of the time (using a Shimadzu 3101 PC). The photocatalytic efficiency was calculated with the Beer–Lambert law, according to [4].

The Water Contact Angle (WCA) test was carried out to evaluate the wettability of the functionalized asphalt mixtures. Using the equipment OCA 15 plus Dataphysics, 3 readings of 5  $\mu$ L water drops were carried out at 2 samples during 2 minutes, at rooms' temperature and relative humidity, and the arithmetic mean was calculated.

### **3 Results and Discussions**

Figure 1a shows all photocatalytic results. The samples only with PTFE (AC 10 PTFE-ETH and AC 10 PTFE-CET) presented a photocatalytic efficiency close to the reference samples (AC 10). The samples with TiO<sub>2</sub> presented a photocatalytic efficiency at least 27% higher than the AC 10 at the end of the test. It can be seen that the best solutions achieved were TiO<sub>2</sub> CET and TiO<sub>2</sub> and PTFE under an ethyl alcohol medium with a concentration of 8 g/L (AC 10 TiO2PTFE-ETH-8g/L).

Figure 1b shows all WCA results. The asphalt mixture AC 10 presented an initial WCA of 117°. All the treated samples presented an increase on the WCA when compared to AC 10. The increase was at least 11% from 117° (AC 10) to 130° (AC 10 TiO2-CET). All the functionalized asphalt mixtures presented а superhydrophobic capability (WCA  $> 150^{\circ}$ ), except those ones with TiO2-W (145°) and TiO2-CET (130°), which presented an overhydrophobic surface ( $120^{\circ} < WCA <$ 150°). Thus, the treatments TiO2-ETH, PTFE-ETH, PTFE-CET. TiO2PTFE-ETH and TiO2PTFE-CET provided the superhydrophobic capability. The best treatment was TiO2PTFE-ETH with a concentration of 8 g/L since it presented one of the highest WCA (154 $^{\circ}$ ) and kept it high longer than the other samples (at least 145° after 20 s). Thus, considering both tests, the best solution was TiO2PTFE-ETH with a concentration of 8 g/L.





Fig. 1. a) Photocatalytic Efficiency Results and b) Water Contact Angle (WCA) Results

## **4** Conclusions

This research aimed to identify the best solution to apply over asphalt mixtures in order to provide them with new capabilities (i.e., functionalization), specifically photocatalytic, superhydrophobic and self-cleaning. For this, different types of solutions were sprayed over a conventional asphalt mixture. Then, the functionalized asphalt mixture samples were submitted to dye degradation for photocatalytic efficiency analysis, and Water Contact Angle (WCA) test. The main conclusions were: i) the coatings with TiO<sub>2</sub> presented a photocatalytic efficiency at least 27% higher than the reference mixture; ii) the best solutions considering this aspect were TiO2-CET and TiO2PTFE-ETH-8 g/L; iii) the treatments TiO2-ETH, PTFE-ETH, PTFE-CET, TiO2PTFE-ETH and TiO2PTFE-CET provided superhydrophobic capability; iv) the best treatment for WCA was TiO2PTFE-ETH 8 g/L; and v) the best solution for both capabilities was TiO2PTFE-ETH 8 g/L. The next step of this research is to spray a coating composed of resin (epoxy, polyurethane, and methyl methacrylate) before the particles' spraying to be placed between the particles and the asphalt mixture. It is aimed to keep the particles immobilized in, to maintain the new capabilities as long as possible.

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