

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, namely photocatalytic, superhydrophobic, and self-cleaning capabilities. Different solutions were prepared combining nano-TiO₂ and micro-PTFE on water, ethyl alcohol, and dimethyl ketone with different concentrations. The solutions were sprayed over the asphalt mixtures, and the photocatalytic and superhydrophobic capabilities were evaluated via decolourization of Rhodamine B dye aqueous solution under simulated solar irradiation and Water Contact Angle (WCA) measurements, respectively. Among the combinations analysed, the best solution was TiO₂-PTFE with ethyl alcohol (8 g/L), which provided a decolourization of about 60% after having spent 8 h in light exposure conditions and a superhydrophobic surface with WCA equal to 153°. Thus, this research work aims to contribute to advances in the field of clean technologies, assisting in the transition to the “Green Recovery”, which is environmentally friendly, inclusive, and sustainable.

1 Introduction

Currently, several research works have contributed to advances in clean technologies, assisting in the transition to an innovative socio-economic model identified as “Green Recovery”, which is environmentally friendly, inclusive, and sustainable. In this sense, the coatings composed of nano/microparticles applied over asphalt mixtures have been provided new capabilities, such as: photocatalytic, to photodegrade pollutants for air cleaning; superhydrophobic, to improve road safety; and self-cleaning, to avoid slipping problems [1,2]. In general, the photocatalytic capability is developed on asphalt mixtures by the application of semiconductor materials, mainly titanium dioxide (TiO₂), by using four significant methods: spraying coating, bitumen modification, volume incorporation, and spreading [3]. In addition to being actual recipients of substantial quantities of nanomaterials, these functionalized asphalt mixtures also act as essential tools for leveraging the emerging industrial segment dedicated to producing materials in the form of nanoparticles.

Road pavements are ideal infrastructures to reduce air pollution levels due to their enormous surface area and their proximity to the pollutant gases (mostly from

vehicles), especially in urban areas [4]. 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_x and SO_x.

The functionalization process 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 these pollutants’ contamination over the road surface [5].

On the other hand, the benefits of providing the superhydrophobic capability to asphalt mixtures are mainly to increase water repellence and prevent ice formation. Therefore, the decrease of friction caused by 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. For this purpose, the literature refers to the application of nano/micromaterials (with a grain size between 6 nm and 45 μm) over asphalt mixtures, namely: TiO₂, ZnO [6], modified-SiO₂ [7], modified fluorine-containing polymer

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with nano-CaO [8], Magnesium–Aluminum layered double hydroxides [9], and PTFE [10]. Usually, for this specific functionalization process, solutions (or dispersions) with these particles are prepared and sprayed over the asphalt mixture surface layer [6,10,11].

Thus, the main objective of this research work is to develop asphalt mixtures with photocatalytic, superhydrophobic, and self-cleaning capabilities. To achieve it, different types of solutions were prepared and sprayed over the asphalt mixture AC 10, namely with TiO₂ and Polytetrafluoroethylene (PTFE) using water, ethyl alcohol, and dimethyl ketone.

2 Materials and Methods

PTFE microparticles with the size of 1 μm were purchased from Merck (Algés, Portugal) while TiO₂ nanoparticles (80% anatase and 20% rutile, particle size is of about 23 to 28 nm) were acquired from Quimidroga (Barcelona, Spain).

First, different types of solutions were prepared with nano-TiO₂ and micro-PTFE with water, ethyl alcohol, and dimethyl ketone using two 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 the solutions over the surface of a conventional asphalt mixture already compacted. The solutions were sprayed over the asphalt mixture samples (8 mL/cm² at room temperature) with the dimensions of 25×25×15 mm³ in order to choose the best solution. The asphalt mixture samples were named by an alphanumeric string, which starts by AC 10 to indicate the asphalt concrete, the particle used (TiO₂ 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 [12,13]. The asphalt mixture samples were immersed into 30 mL of RhB aqueous solution with a concentration of 5 ppm. The systems were placed inside a box containing a sunlight simulation lamp, located 25 cm above the samples, resulting in a power intensity of 11 W/m². First, the samples were kept in dark condition for 3 h and then they were irradiated during 8 h. In this way the adsorption and photocatalysis phenomena could be split and the photocatalytic efficiency could be better analysed. To avoid variations in concentration due to the evaporation of RhB solution, 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⁻¹) of the dye was evaluated as function of the time (using a Shimadzu 3101 PC). The photocatalytic

efficiency (Φ) was calculated with the Equation 1, according to [5].

$$\Phi (\%) = \left(\frac{A_0 - A}{A_0} \right) \times 100 \quad (1)$$

Where A and A₀ represent the maximum absorbance of RhB solution for time “t” and 0 hour, respectively.

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 μL water drops were carried out at 2 samples for 2 minutes, at room temperature and relative humidity, and the arithmetic mean was calculated. Surfaces with WCA higher than 150° present superhydrophobic capability [6,10,11,14].

3 Results and Discussions

Figure 1 shows the results of the photocatalytic essay. A global examination of these results reveals that the samples only with PTFE (AC 10 PTFE-ETH and AC 10 PTFE-CET) presented a photocatalytic efficiency 21% higher than AC 10. In addition, the samples with TiO₂ showed a photocatalytic efficiency at least 38% higher than the AC 10 at the end of the test, with the worst performing results for the sample AC 10 TiO₂PTFE-CET-4g/L, which increased the efficiency from 34% to 47% (38% increase), when at least TiO₂ is used.

When ketone was used, the highest efficiencies were achieved with only TiO₂. Besides that, when the ethyl alcohol was used, the best treatment was AC 10 TiO₂PTFE-ETH-8g/L, then AC 10 TiO₂-ETH and AC 10 TiO₂PTFE-ETH-4g/L. The effect of the solvent on the efficiency of samples with TiO₂ in decreasing order of performance was ketone followed by ethyl alcohol and water, with almost the same results.

For the combination of the particles, the increase of the photocatalytic efficiency was 5% for the ethyl alcohol and 15% for the ketone, when the concentration increases from 4g/L and 8 g/L. It can be seen that the best solutions achieved were TiO₂-CET and TiO₂-PTFE under an ethyl alcohol medium with a concentration of 8 g/L (AC 10 TiO₂PTFE-ETH-8g/L).

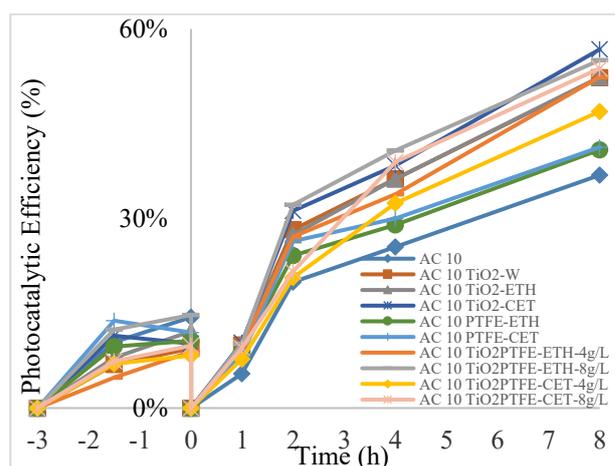


Fig. 1. Photocatalytic efficiency results.

Figure 2 shows the WCA results. All the treated samples increased WCA when compared to AC 10. The increase was at least 11% concerning the AC 10 TiO₂-CET sample. All functionalized asphalt mixtures presented a superhydrophobic capability (WCA > 150°), except TiO₂-W (145°) and TiO₂-CET (130°), which are overhydrophobic surfaces (120° < WCA < 150°) [6,10,11,14]. Thus, the treatments TiO₂-ETH, PTFE-ETH, PTFE-CET, TiO₂PTFE-ETH, and TiO₂PTFE-CET provided superhydrophobic capability.

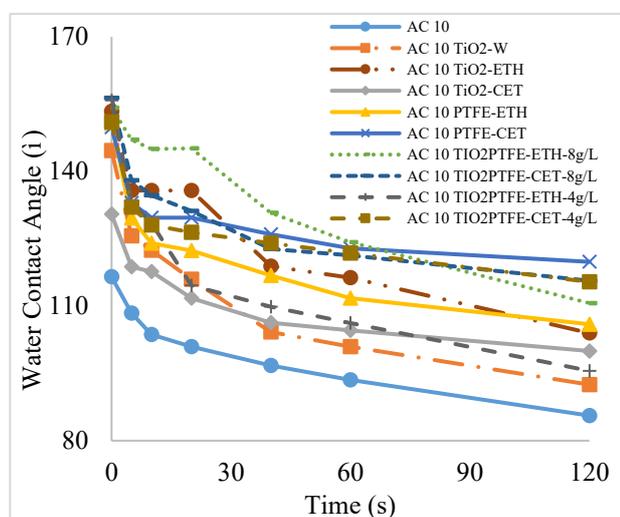


Fig. 2. Water Contact Angle results.

Regarding the effect of the solvents with TiO₂, ethyl alcohol led to the best WCA (153°), followed by water (145°). The worst of them was with ketone (130°), as already mentioned before. For the PTFE, both ketone and ethyl alcohol treatments presented similar initial results, but with time, the best of them was with ketone.

The increase in the concentration of TiO₂-PTFE was more effective on the ethyl alcohol. For the whole testing, doubling the concentration leads to an increase of the WCA of 13% and 2% for ETH and CET, respectively.

When the particles were combined, the initial WCA was similar (155°), except for AC 10 TiO₂-PTFE-CET-4g/L, that was slightly less (151°). Nevertheless, considering the whole testing duration, it is clear that samples with higher WCA were the AC 10 TiO₂PTFE-ETH-8g/L. The average of WCA from 0 to 120 s increase 36% when compared to the reference sample. This same functionalized asphalt mixture showed a WCA at 20 s, and a better performance than all the other samples, that dropped the WCA to at least 131°, along this testing time. As explained before, the best results are represented by the highest initial WCAs.

For the same solvent, solutions with TiO₂ and PTFE and a concentration of 8 g/L delivered the highest WCA. While the results for the solutions with ketone were similar except for TiO₂-CET (the worst of them), for ethyl alcohol, the results were dispersed over time.

Thus, the treatment TiO₂PTFE-ETH-8g/L was the best solution since it was the best considering the WCA and the second one regarding photocatalysis. The best one

regarding the photocatalytic efficiency (AC TiO₂-CET) presented the worst WCA for the treated samples. While the second best considering the WCA (AC 10 TiO₂PTFE-ETH-4g/L) was the fifth performance concerning the photocatalysis. Thus, considering both tests, the best solution was TiO₂PTFE-ETH with a concentration of 8 g/L.

4 Conclusions

This research aimed to identify the best solution to apply over asphalt mixtures to provide them with new capabilities, 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:

- The coatings with at least TiO₂ presented a photocatalytic efficiency at least 38% higher than the reference mixture without any treatment;
- The best solutions considering this aspect were TiO₂-CET and TiO₂PTFE-ETH-8 g/L;
- The treatments TiO₂-ETH, PTFE-ETH, PTFE-CET, TiO₂PTFE-ETH, and TiO₂PTFE-CET provided superhydrophobic capability;
- The best treatment for WCA was TiO₂PTFE-ETH 8 g/L;
- The best solution for both capabilities was TiO₂PTFE-ETH 8 g/L.

It is important to emphasize that these functionalized asphalt mixtures can degrade gases like SO_x and NO_x, avoid road accidents by cleaning the dirt particles and degrade oils/greases over their surface, presenting benefits to road safety and the environment. In this sense, the present work showed that one of the potential destinations for the large-scale application of nanomaterials is the civil engineering, especially road construction. Furthermore, this destination assists in promoting the dynamism and commercial progress of nanomaterial and nanotechnology industries.

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