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Functionalized Asphalt Mixtures: Photocatalytic, Superhydrophobic and Self-cleaning Properties

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Abstract

Functionalization of road pavement asphalt mixtures provides new capabilities that can mitigate problems like air pollution and road accidents. In this research, nano-TiO_2 and micro-ZnO were deposited through an aqueous solution by spraying it over the surface of asphalt mixture samples in order to promote the photocatalytic, superhydrophobic and self-cleaning capabilities. Tested by degradation of Rhodamine B, to assess the Photocatalytic Efficiency, and by Water Contact Angle (WCA), to assess the wettability of the materials, this technique can be used to promote these multifunctional capabilities in asphalt mixtures. With these enhanced surface characteristics, road safety and the environment, through pollutants degradation like NO_x and SO_2, will be improved.

Author Keywords. Photocatalysis, Superhydrophobic, Self-cleaning, Asphalt mixtures.

1. Introduction

Nowadays air pollution is one of the biggest environmental problems. The demand for the development of less harmful techniques is continuous as can be perceived by the number of Climate Change Conferences held at world level.

Road traffic is one of the most important sources of pollution which makes vehicles and also the road itself targets to reduce pollution. Asphalt mixtures are the materials used the most in road pavement surface courses. The superficial characteristics of this material are very important during the life cycle of the pavement due to their interaction with vehicles' tyres. They are very important to road safety particularly on wet conditions. The worst weather condition occurs when there is water or ice on the pavement surface. Thus, it is important to drain or repel the surface water quickly aiming at reducing the number of road accidents. Moreover, roads are close to vehicles and they have a large area.

In this context, the integration of nano/microparticles in asphalt mixtures will provide the road surfaces with new capabilities (functionalization) such as: (i) photocatalytic: able to photodegrade pollutants for the purpose of cleaning the environment; (ii) superhydrophobic: better water resistance and greater road safety in periods of rains and low temperatures; (iii) self-cleaning: avoid slipping problems, facilitate the water drainability and prevent the pore fouling phenomenon.

The photocatalytic activity of titanium dioxide (TiO_2) was studied for the first time by Fujishima and Honda (1972) (FUJISHIMA and HONDA 1972). Asphalt mixtures with photocatalytic properties can promote air purification by oxidation of pollutant agents (Carneiro et al. 2013). Semiconductor oxides, like TiO_2 and ZnO, have the ability to oxidize gases in the presence of light and humidity, such as NO_x, SO_2 and to degrade organic pollutants.

The literature review about photocatalytic capacity applied in asphalt mixtures address the following subjects: photocatalytic capacity of Hot Mix Asphalts (Toro et al. 2016; Carneiro et al. 2013), Warm Mix Asphalts (Hassan et al. 2012) and Asphalt Emulsions (Bocci et al. 2016); Application in real context (Dylla et al. 2013; Liu et al. 2015; Bocci et al. 2016); Computational modeling of the photocatalytic capacity of road pavements (Dylla et al. 2013).

The technique of surface spraying of nanoparticles aqueous solution presents higher efficiency when compared with the bulk incorporation or with the bitumen modification (Carneiro et al. 2013; Toro et al. 2016; Hassan et al. 2012). The photocatalytic property is affected by: (i) application: rate of application (mg/cm^2); (ii) environmental issues: intensity of UV light (mW/cm^2), relative humidity (%), pollutant flow (L/min) (environmental pollution) (Dylla et al. 2013; Melo and Trichês 2012; Hassan et al. 2012; Carneiro et al. 2013).

Superhydrophobic materials can repel the water very quickly and the self-cleaning property provides the superficial cleaning (Arabzadeh et al. 2016). This characteristic is correlated to the surface morphology and roughness of the materials. Other advantages of the superhydrophobic asphalt mixtures would be to repel water and ice, being less sensitive to moisture damage and they will probably improve binder-aggregate adhesion. This property can also avoid the pore clogging (fill of voids by dirt particles) in porous asphalt mixtures.

Generally, the contact angle between water and surface (Water Contact Angle – WCA) is used to measure the wettability of a material. There are four surface classifications (Muzenski, Flores-Vivian, and Sobolev 2015): (i) hydrophilic: WCA < 30°; (ii) Hydrophobic: 90°< WCA< 120°; (iii) Overhydrophobic: 120°< WCA < 150°; (iv) Superhydrophobic: WCA > 150°. Cassie-Baxter (1945) model, considered the best model for asphalt mixtures by Nascimento et al. (2012), takes in account that the water drop is suspended on the surface microgeometry.

The self-cleaning capability developed in new materials is shown, on the one hand, by the ease that water droplets roll on the surfaces and carry the dirt previously deposited, based on the effect of the lotus flower (superhydrophobic). Also considered as a self-cleaning characteristic, water droplets are spread on the surface (superhydrophilic), which is easier washed by removing adsorbed dirt on its surface during rainy periods. On the other hand, by the fact that the photocatalytic materials can degrade organic pollutants (like oils), these materials could also be classified by self-cleaning materials.

2. Materials and Methods

The photocatalytic, superhidrophobic and self-cleaning properties are provided to the asphalt mixture by spraying on the surface at 60°C an aqueous solution with nano-TiO_2 and micro-ZnO. To assess these properties photocatalytic efficiency and water contact angle tests were carried out (see Figure 1).

TiO_2 and ZnO are semiconductors with low toxicity, low price and high stability (Dalton et al. 2002; Pickett et al. 2017). TiO_2 can be found in 3 mineral compounds: anatase, rutile and brookite (Kaplan et al. 2016). The anatase form shows the highest efficiency in photocatalytic capacity when compared with rutile and brookite (Bilmes et al. 2000). On the hand, ZnO usually crystallizes in two forms: cubic zincblende and hexagonal wurtzite structures. The semiconductors were combined to improve the photocatalytic efficiency.

The aqueous solution (pH 8) was composed of 4g/L of nano-TiO_2 and 1g/L of micro-ZnO. The spraying rate was between 5 mg/cm^2 and 12,5 mg/cm^2.

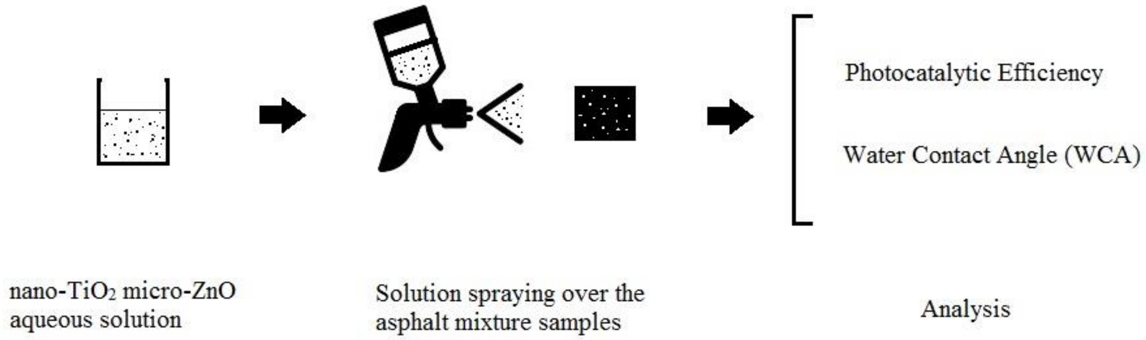

Figure 1: Methodology

The asphalt mixture sample (25x25x15 mm^3), designated by AC 6 surf Elaster 13/60 (Marshall design), was composed of 6% of bitumen Elaster 13/60 and aggregate fractions of 3% of limestone filler, 25% of 0/4 mm aggregate and 72% of 4/6 mm aggregate. It is composed mostly of intermediate aggregates (4/6) and commercial asphalt binder, which is modified by SBS. It also has a high volume of voids.

The measurement of the absorption of a dye on an aqueous solution as a function of irradiation time allows to analyze the photocatalytic and self-cleaning properties. In this work, Rhodamine B (RhB) was used for this propose. The decrease of maximum absorbance indicates the degradation of RhB with light according to Beer-Lambert law (Carneiro et al. 2013). Each asphalt mixture sample was immersed in 30mL of RhB aqueous solution (5ppm). After 6h in dark condition, the samples were irradiated with a 300 W - OSRAM Ultra-Vitalux lamp, placed at 25 cm from the sample. The RhB solution absorbance was measured using a Shimadzu 3101 PC spectrophotometer during 8h. For testing AC 6 with and without TiO_2 ZnO treatment, 3 samples were used. The photodegradation efficiency (Φ) was calculated by the average of percentage of absorbance decreasing (at 554nm) by Equation 1 (Carneiro et al. 2013). Besides this, the reaction rates (k) (first-order reaction) were calculated in order to measure the reaction velocity (Equation 2).

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

$$k = -\frac{1}{t} \times \ln\left(\frac{A_t}{A_0}\right) \quad (2)$$

Where t is time, A_t and A_0 represent the absorbance for time t and 0 hour, respectively.

Finally, the water drop contact angle allows the measurement of superficial wettability, making possible the analysis of superhydrophobic and also self-cleaning properties. The first angle was determined for a 5µL water drop in contact with surface using the equipment OCA 15 plus dataphysics considering the Cassie-Baxter (1945) model (Nascimento et al. 2003). It was measured 3 times on AC 6 samples with and without TiO_2 ZnO treatment. The average values for each case were considered for analysis.

3. Results and discussion

Figure 2 shows the photocatalytic efficiency for the samples with and without TiO_2 ZnO treatment. Before irradiation, when the molecules of RhB adhere and are retained on the samples, the adsorption of the dye was low and almost the same for both mixtures. After 2h of irradiation, it was possible to observe differences in the photocatalytic efficiency. After 8h, the efficiency of the sample with the TiO_2 ZnO treatment was 2,4 times higher than the one without treatment. The efficiency determined for AC 6 without treatment was probably due to the semiconductors naturally present on the exposed aggregates.

Table 1 shows the reaction rates of the photocatalysis. In the beginning of the process, after 0,5 hours of irradiation, the reaction rate was the highest for both mixtures. After 8 hours of irradiation, the reaction rate of the functionalized mixture was almost 3 times higher than the not functionalized.

Thus, it was possible to prove the photocatalytic and self-cleaning capacity of the functionalized asphalt mixtures.

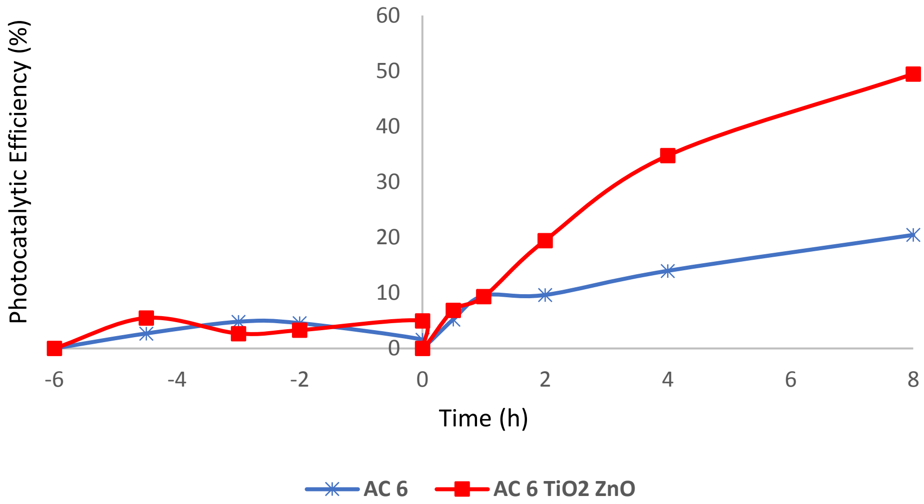

Figure 2: Photocatalytic Efficiency

Time (h)	Reaction Rate ($10^{-3}min^{-1}$)	
	AC 6	**AC 6 TiO_2 ZnO**
0	0.0	0.0
0.5	1.8	2.4
1	1.7	1.6
2	0.8	1.8
4	0.6	1.8
8	0.5	1.4

Table 1: Reaction Rate

The analysis of the asphalt mixture wettability is based on the measurement of the contact angle between a water drop and the asphalt surface. Figure 3 shows the form of the drops for the samples with and without TiO_2 ZnO treatment. The spherical form of the drop is noticed only when the treatment was applied. The contact angle for the functionalized samples was 153° while for the other was 102°. Therefore, the superhydrophobic property is guaranteed for samples sprayed with TiO_2 ZnO (Figure 3).

a) b)

Figure 3: Water Contact Angle Image: a) AC 6; b) AC 6 TiO_2 ZnO

4. Conclusions

This work aimed to provide photocatalytic, superhydrophobic and self-cleaning properties to asphalt mixtures. This was achieved by spraying a nano-TiO_2 micro-ZnO aqueous solution over an AC 6 asphalt mixture. The immediate impact of these new capabilities are, on the one hand, environmental and, on the other hand, safety related. They will guarantee that roads are safer and greener through the degradation of pollutants, mainly NO_x and SO_2, mitigating air quality problems in metropolitan areas and avoiding the greenhouse effect and acid rains. The superhydrophobic property of these mixtures will be responsible to repel and drain the water faster in order to reduce the water film between tires and the road surface. In addition, it is expected to avoid ice formation over the surface during winter. Due to the self-cleaning property, the number of accidents can be reduced by removing the small dirt particles drained with water (lotus effect) and degrading oils on the pavement surface and also it also expected to prevent pore clogging which happens in open graded asphalt mixtures.

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