

# Photocatalytic Asphalt Mixtures: Semiconductors' Impact in Skid Resistance and Microtexture

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## ABSTRACT

Photocatalytic and self-cleaning asphalt mixtures have the capacity of mitigating air quality problems and degrade oils/greases. Their functional characteristics can change due to the presence of semiconductors. Thus, after the application of semiconductors on asphalt mixtures, the assessment of skid resistance and microtexture becomes important since they are essential to assure safety. Photocatalytic and self-cleaning were provided to two types of mixtures by spraying and bulk incorporation. Pendulum Tests were carried out in AC 14 and AC 6 at 5 temperature levels in dry and wet conditions. Their microtexture was evaluated by optical non-contact rugometric characterization. The results show that, in dry condition, the skid resistance of functionalized asphalt mixtures was similar to the mixes without treatment. In wet condition, the functionalization caused a maximum decrease of 7% in skid resistance. The semiconductors influenced only the skewness of AC 14 with 6% TiO<sub>2</sub> when bulk incorporated. All the other amplitude parameters were not affected by the functionalization. Furthermore, the application of the semiconductors can be used without high impacts in microtexture and therefore in friction.

**Keywords:** Photocatalytic Asphalt Mixtures, Microtexture, Skid Resistance, Optical Non-Contact Rugometric Characterization.

## 1. INTRODUCTION

Functionalization is the development of capabilities for the materials, different of the essential ones, usually related to the surface. Implemented by semiconductors, photocatalytic and self-cleaning asphalt pavements can decrease the atmospheric concentration of gases NO<sub>x</sub> and SO<sub>2</sub>, mitigating air pollution [1,2]. Moreover, these materials can, by self-cleaning property, degrade organic compounds (oils and greases), removing them from the surface in order to have safer roads [3]. This is possible by the heterogeneous photocatalytic process, which results from the absorption of photons with energy equal to or greater than the band gap of the semiconductor, exciting the electrons, which go from the valence band to the conduction band. This migrate generates an electron/hole pair (e<sup>-</sup>/h<sup>+</sup>). e<sup>-</sup> and h<sup>+</sup> provide oxidation-reduction reactions, forming respectively

1 hydroxyl ( $\text{HO}^*$ ) and superoxides ( $\text{O}_2^-$ ) radicals in the presence of water and oxygen molecule. They  
2 react with the pollutants presented over the surface, degrading them [4,5].

3 In general, three approaches have been carried out to develop the photocatalytic asphalt  
4 pavements: i) spraying deposition; ii) bulk incorporation; and iii) bitumen modification. The first  
5 technique is the most efficient using less semiconductors. The second one probably has the best  
6 fixation but more material is necessary. The last one allows the analysis of bitumen properties  
7 concerning the impact of the semiconductors [3,6,7]. After the application of the semiconductors  
8 on asphalt mixtures, the assessment of skid resistance and also microtexture becomes important.  
9 This process should at least maintain the essential functional characteristics.

10 The main functional characteristics, which contribute to safety, comfort and environmental  
11 issues, are: tyre-road noise, friction, texture (divided in micro, macro, megatexture and roughness),  
12 drainability and rolling resistance. The skid resistance is the friction force developed at the contact  
13 of tyre and pavement [8,9]. The friction decreases when pavements are wet, generating the worst  
14 contact conditions between the tyre and the pavement motivated by the difficulty of water  
15 drainage. The friction is higher in the winter than in the summer due to the viscosity of the asphalt  
16 binder and the performance of the tyres [10,11]. The microtexture has a very high influence on  
17 friction. This microtexture refers to ranges of spatial wavelengths up to 0.5 mm and of amplitudes  
18 up to 0.2 mm. This characteristic is provided mainly by the roughness of the aggregates which  
19 become polished with traffic loading [8]. Due to the scale, it is difficult to acquire microtexture,  
20 therefore, the use of an optical triangulation based optical microtopographer equipment became  
21 important. This technique allows, by its inherent relative simplicity robustness and reliability, the  
22 sound metrological inspection of objects' surfaces, making possible to access microtopography  
23 and calculate several roughness parameters [12,13].  
24

## 25 2. MATERIALS AND METHODS

26 In this research, two asphalt mixtures, by Marshall design, were evaluated: AC 14 Surf  
27 35/50 and AC 6 Surf Elaster 13/60 slabs, composed by 5% and 6% of binder, respectively. The  
28 aggregate composition of the mixtures was: AC 6 (limestone filler: 3%; 0/4 mm: 25% and 4/6 mm:  
29 72%), AC 14 (limestone filler: 3%, 0/4 mm: 41%, 4/8 mm: 12% and 6/14mm: 44%). Table 1  
30 identifies the mixtures analysed in this research, how the semiconductors were applied, the  
31 Maximum Bulk Density (MBD) and the Void Content (VC) of the mixes.  
32  
33

34 **TABLE 1 Properties of Asphalt Mixes**

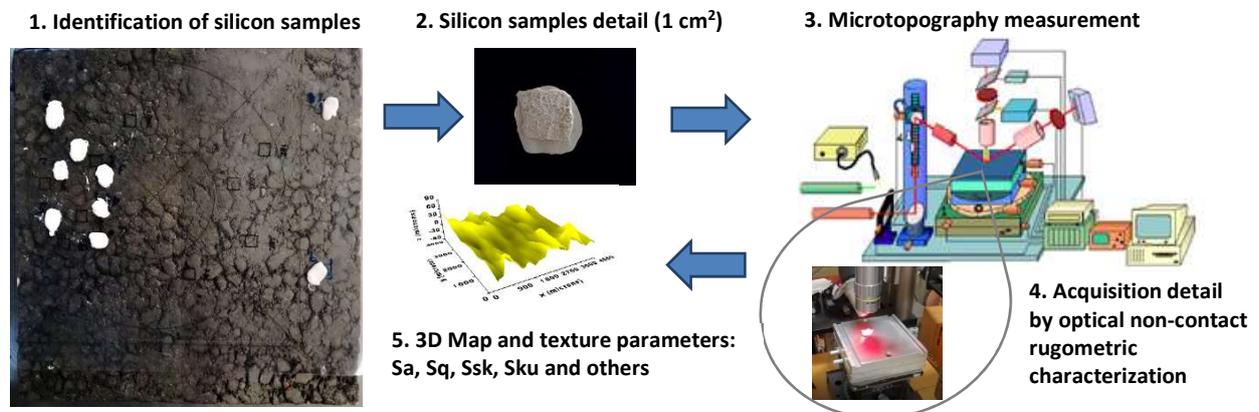
Asphalt mix	Semiconductors	Technique	MBD ( $\text{g}/\text{cm}^3$ )	VC (%)
AC 6	$\text{TiO}_2$ and/or ZnO	Spraying	2.423	10.9
AC 14	$\text{TiO}_2$ and/or ZnO	Spraying	2.426	4.4
AC 14 3%	3% $\text{TiO}_2$	Bulk incorporation	2.377	3.8
AC 14 6%	6% $\text{TiO}_2$	Bulk incorporation	2.356	4.4

34 The photocatalytic and self-cleaning properties were provided to the asphalt mixtures by:  
35 i) spraying on the surface for AC 14 and AC 6; and ii) bulk incorporation with 3% and 6% of  $\text{TiO}_2$   
36 for AC 14. An aqueous solution of nano- $\text{TiO}_2$  (4 g/L) and/or micro-ZnO (1 g/L) with pH 8 was  
37

1 sprayed covering the rate of 5 mg/cm<sup>2</sup> to 12.5 mg/cm<sup>2</sup> over AC 6 and AC 14 mixes at 60 °C. The  
 2 functionalization by bulk incorporation was achieved by partially replacing the filler with 3% and  
 3 6% of TiO<sub>2</sub> in mass of the bitumen, resulting in 2.84% and 2.68% of filler respectively. The bulk  
 4 incorporation technique has a much higher cost than the spraying coating due to the higher amount  
 5 of material used.

6 In order to access the friction of the mixes before and after the application of the  
 7 semiconductors in wet and dry conditions at 5 different temperatures, 100 Pendulum tests (results  
 8 in Pendulum Test Value – PTV) were carried out (EN 13036-4). This test is one of the most popular  
 9 to determine friction and is widely used to analyse small samples of asphalt mixtures in laboratory  
 10 and also highway pavements in specific conditions. For highways, this test is still used, through  
 11 punctual measures, due to the low cost and easy operation [10]. To perform the wet procedure, the  
 12 water and the pavement were conditioned at the same temperature, which made possible the  
 13 control of the system temperature.

14 To measure the microtexture an optical microtopographer was used. With large measuring  
 15 range, high versatility, robustness and reliability, good accuracy and resolution, the  
 16 MICROTOP.06.MFC microtopographer is used to inspect a large range of surface types [12,13].  
 17 The system is based on discreet active triangulation. The surface is scanned by an oblique light  
 18 beam. The point-by-point scanning of the sample is carried out by the movement of a precision  
 19 XYZ displacement on a rectangular array separated by distances down to 1.25 μm. By triangulation  
 20 sensing of the reflected light at each scanning position, a full 3D inspection of the sample is  
 21 achieved. In each asphalt mixture slab, 9 squares with 1 cm<sup>2</sup> were identified to acquire in that area  
 22 the microtexture. In total, 90 microtexture silicone casts were done (Figure 1) to carry out the  
 23 microtopography measurement of 4 mm<sup>2</sup> area [12].



24  
 25 **FIGURE 1. Microtexture Achievement Procedure**  
 26

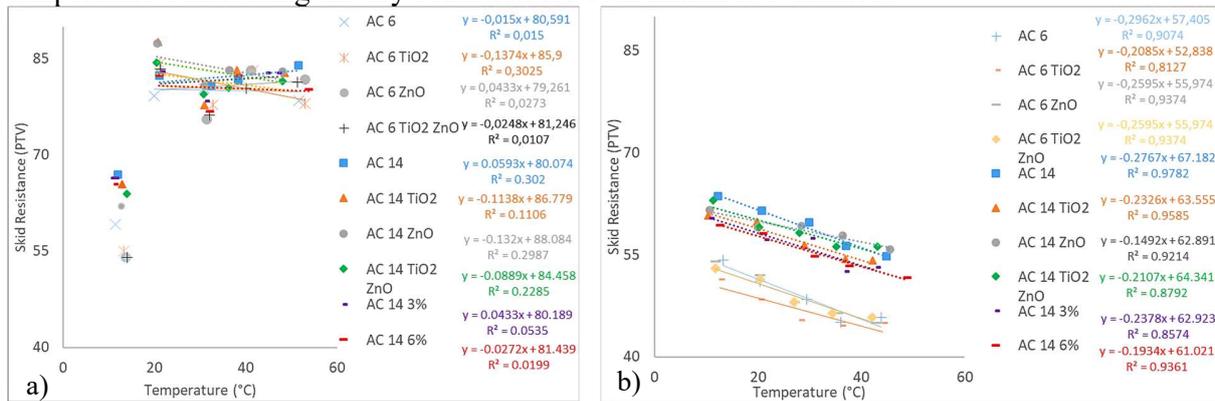
27 In order to analyse the microtexture of the surfaces the main roughness parameters Average  
 28 roughness or Arithmetic Mean Deviation of the Surface (Sa), Root-mean-square Deviation of the  
 29 Surface (Sq), Total Height of the Surface (St), Maximum Peak Height of the Surface (Sp),  
 30 Maximum Valley Depth of the Surface (Sv), Ten-point Height roughness of the Surface (Sz), Ssk  
 31 (Skewness) and Sku (Kurtosis) were obtained. The parameters Sa and Sq were used to quantify  
 32 significant deviations of textures. The symmetry of peaks and valleys of the surface about the  
 33 average surface is established by Ssk for: i) Ssk = 0: normal distribution, that is, symmetry about  
 34 the average line; ii) Ssk < 0: predominance of valleys (negative texture); iii) Ssk > 0: indicates  
 35 higher number of peaks (positive texture). The Kurtosis Sku characterizes the presence of  
 36 extremely deep valleys/high peaks (for: i) Sku = 3: normal distribution; ii) Sku > 3: extremely deep

1 valleys/high peaks; iii)  $Sku < 3$ : lack of them). ANOVA analysis (factors: mixture and treatment)  
 2 was carried out to determine if there is an interaction effect between the independent variables (Sa,  
 3 Sq, St, Sp, Sv, Sz, Ssk and Sku) over the parameters for a significance level of  $(1 - \alpha = 0.1)$ .  
 4 Bonferroni Post-Hoc analysis was also carried out in order to find patterns between subgroups. It  
 5 analyses if there is a significantly difference of the average of parameters between the samples.

## 6 3. RESULTS

### 7 3.1 Skid Resistance

8 Figure. 2 shows the results of the skid resistance and the linear regression fit parameters  
 9 for each material. In dry condition, the skid resistance of functionalized asphalt mixtures was  
 10 similar to the mixes without treatment. The AC 6 showed PTV values 2% lower than the AC 14,  
 11 except for the lowest temperature. At the lowest temperature, the surface was probably wetted by  
 12 condensed water during the conditioning procedure, reducing the PTV value to those similar to  
 13 the wet condition. The  $R^2$  values were less than 0.35, indicating a poor relation between PTV and  
 14 temperature considering the dry condition for both mixtures evaluated.



15 **FIGURE 2. Results of Pendulum Test: a) Dry Condition and b) Wet Condition**

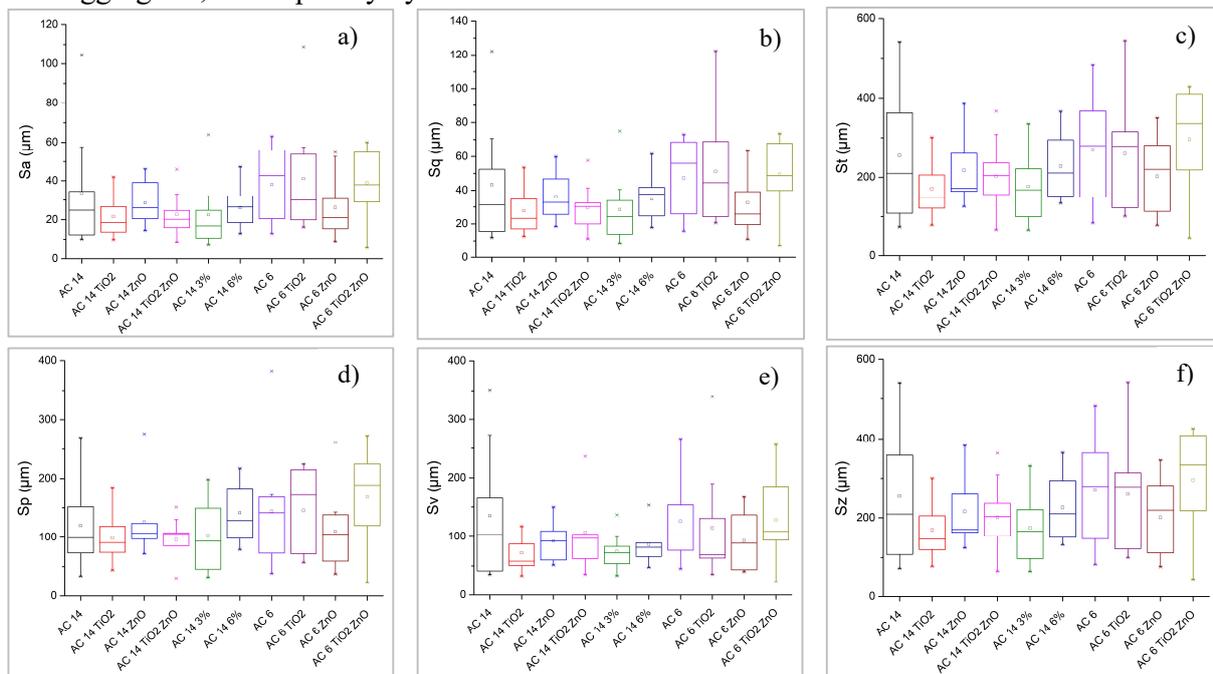
16  
 17 In wet conditions, when comparing the trend lines, the application of semiconductors on  
 18 AC 14 did not have a great impact on friction. The higher temperature sensitivity was 6% for AC  
 19 14 with 6 PTV values of difference (9%) comparing its linear coefficient to the linear coefficient  
 20 of AC 14. For AC 6, the trend lines almost overlap, except for AC 6 TiO<sub>2</sub>. For both mixtures, the  
 21 minimum and maximum differences in PTV after spraying were between -6% (TiO<sub>2</sub> at 29 °C) and  
 22 3% (ZnO at 36 °C and TiO<sub>2</sub> ZnO at 43 °C). When the TiO<sub>2</sub> semiconductor was applied by bulk  
 23 incorporation, the minimum and maximum differences in PTV was -7% (AC 14 3% at 22 °C) and  
 24 2% (AC 14 6% at 38 °C). To summarize, for spraying technique the maximum absolute difference  
 25 was 6%, corresponding to a decrease from 48 to 45. For bulk incorporation, the maximum absolute  
 26 difference was 7%, corresponding to a decrease from 61 to 57 PTV. The AC 6 mixture had in  
 27 average a friction 16% lower than the AC 14 mixture. This result indicates that the friction is  
 28 higher for mixtures with higher nominal maximum aggregate size, in accordance with the results  
 29 for asphalt concretes by Wang et al. (2011) [14]. A linear trend of PTV and temperature was  
 30 established with  $R^2$  higher than 0.80. The friction was inferior for higher temperatures than it was  
 31 for lower temperatures. This conclusion is in accordance with Bazlamit et al. (2005) results [11].  
 32 The AC 14 presented values of  $R^2$  higher than that of the AC 6 mixture. The angular coefficient  
 33 of the trends, on average, was -0.22 for AC 14 and -0.27 for AC 6, which shows that AC 6 was

1 more sensitive to temperature. The type of surface was a more important factor when the pavement  
 2 is wet comparing the differences with and without water.

3 In conclusion, there is no increasing or decreasing trend of friction with temperature after  
 4 the addition of the semiconductors when applied by spraying an aqueous solution or bulk  
 5 incorporation. AC 6 was less influenced by the semiconductors when sprayed, which may have  
 6 resulted from the higher porosity of the mixture. Also, either in dry or wet condition, the  
 7 semiconductors did not cause a high impact in the friction of the asphalt mixtures. This is important  
 8 since the promotion of the new capacity did not cause a big impact in the most important functional  
 9 characteristic of the pavement surfaces analysed.

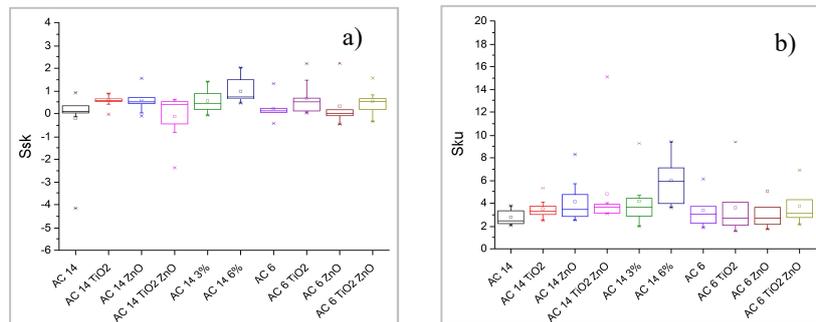
### 11 3.1 Microtexture

12 Figure 3 shows the results of Sa, Sq, St, Sp and Figure 4 the ones of Sv, Sz, Ssk and Sku of  
 13 the microtexture assessment. A major dispersion of values was registered, except for Ssk and Sku.  
 14 In general, the results of AC 6 were more dispersed values than the results of AC 14. Probably it  
 15 happened due to the difficulty in selecting the sampling area which is influenced by the smaller size  
 16 of the aggregates, consequently by its macrotexture.



17 **FIGURE 3. Microtexture Results: a) Sa, b) Sq, c) St, d) Sp, e) Sv and f) Sz**

18  
 19 The results show a normal distribution ( $Sku = 3$ , included between the first and third  
 20 quartiles), except for AC 14 TiO<sub>2</sub>, AC 14 TiO<sub>2</sub> ZnO and AC 14 6%. These 3 mixture combinations  
 21 have the first quartile higher than 3, identifying extremely deep valleys/high peaks. Regarding Ssk,  
 22 the mixtures had the first quartile higher than 0, excluding AC 14 6% and AC 6 TiO<sub>2</sub>, indicating  
 23 only positive values, thus all of them conducting to a positive microtexture, and AC 14 6% and  
 24 AC 6 TiO<sub>2</sub>, with a negative first quartile and positive third quartile (normal distribution).



**FIGURE 4. Microtexture Results: a) Ssk and b) Sku**

By ANOVA, on one hand the independent variable Mixture had a significant influence on Sa, Sq, Sp, St and Sz ( $p < 0.1$ ). On the other hand, the variable, Treatment, had a significant influence only on Ssk. The interaction of Mixture and Treatment variables had no significant effect on the dependent variables results. The Bonferroni Post-Hoc test for a level of significance ( $1 - \alpha = 0.1$ ) was carried out as well. The average of Sa, Sq, St, Sp, Sz for the AC 14 samples was significantly lower than the AC 6 samples ( $p < 0.1$ ). AC 6 had more dispersed microtexture, higher peaks and ten-point heights than AC 14. It can be concluded that the skid resistance was determined by the larger contact area of the macrotexture. Furthermore, the microtexture assessment for AC 6 was mostly carried out over intermediate aggregates and AC 14 was carried out over fine aggregates bonded with binder and coarse aggregates, conducting to a smooth surface. For the different treatments, the PostHoc test carried out showed just one difference on the average of the independent variables. The average of Ssk for the AC 14 6% was significantly lower than the AC 14 ( $p < 0.1$ ). Lastly, the asphalt mixture type was an important factor for the microtexture and the functionalization had a low impact in this characteristic.

## CONCLUSIONS

This research aimed to analyse the friction and the microtexture of different asphalt mixtures after functionalization by spraying and bulk incorporation. In dry condition, the asphalt mixtures had similar friction independently of the temperature. In wet condition, AC 6 had a PTV 16% lower than the AC 14 mixture and was also more sensitive to temperature. The surface was a more important factor when the pavement is wet, comparing the wet and dry friction. The functionalization by spraying conducted to a difference in PTV between -6% and 3%. By bulk incorporation, this interval of difference was -7% and 2%. For microtexture, the asphalt mixture had a significant influence only on Sa, Sq, Sp, St and Sz. The average of Sa, Sq, St, Sp, Sz measurements of the AC 14 was significantly lower than the AC 6. AC 6 had more dispersed microtexture, higher peaks and ten-point heights than AC 14. It can be justified by the AC 14 microtexture assessment, which was carried out also over fine aggregates bonded with binder, conducting to a smoother surface. Only the average of the parameter Ssk of the AC 14 6% was significantly lower than the AC 14 samples ( $p < 0.1$ ). In conclusion, the treatments did not affect the amplitude parameters of microtexture. Thereby, the functionalization had a low impact in the friction and the microtexture, allowing the application of the semiconductors by bulk incorporation and spraying. The next steps of this research should be the assesment of microtexture and friction on differet types of photocatalytic road surfaces after several levels of traffic wearing in laboratory and in a experimental section built in real context.

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