Are There New Ways to Improve the Asphalt Mixtures' Surface Functions? For Sure! By Functionalization Process

Iran Rocha Segundo[1], Cátia Afonso[2], Orlando Lima Jr.[1], Salmon Landi Jr.[3], Elisabete Freitas[4,*], and Joaquim O. Carneiro[2]

[1] *University of Minho, ISISE*
[2] *University of Minho, CF-UM-UP*
[3] *Federal Institute Goiano*
[4] *Corresponding Author; University of Minho, ISISE.* efreitas@civil.uminho.pt

ABSTRACT. Titanium Dioxide (TiO_2) semiconductor material and Polytetrafluorethylene (PTFE) have been applied in the form of nano/microparticles over asphalt road pavements to provide them with new surface functionalities. This is a functionalization process that aims to improve the sustainable characteristics of the asphalt mixtures through the photocatalytic, superhydrophobic, and self-cleaning capabilities, which are related to the degradation of hazardous pollutants from the atmosphere (NOx, SO2, among others) for environmental remediation and the cleaning of the road surface (dust, greases, and oils) for the mitigation of the decrease of friction. Thus, in this research work, dispersions containing TiO_2 nanoparticles and PTFE microparticles were sprayed over an AC 10 asphalt mixture to coat and functionalize it. To confirm the photocatalysis, super hydrophobicity, and self-cleaning capacities, this smart material performance was evaluated under the degradation of the organic compound Rhodamine B (RhB) as a pollutant model and Water Contact Angle (WCA). The results indicate the photodegradation of the pollutant, confirming the proper functioning of the functionalization process, and a WCA of 150 °, proving that the nanoparticles were well dispersed just over the surface of the asphalt mixture. In general, this multidisciplinary research contributes to social and environmental enhancement and enlarges the opportunities for applications of nanomaterials in a very large-scale field such as Civil Engineering. Moreover, it showed that the surface characteristics of the asphalt pavements could be studied and improved not only with a conventional approach based on noise, friction, texture, and rolling resistance measurements but also through a physicochemical approach, as the functionalization processes, using knowledge of Materials Science.

Keywords. Functionalized Asphalt Mixtures, Photocatalysis and Self-Cleaning, Surface Characteristics, Smart Coatings, Sustainable Road Pavements.

Introduction

Recently, new capabilities have been applied to several materials, including Civil Engineering materials, such as asphalt mixtures (Segundo et al. 2021). New capabilities such as photocatalytic (Hassan et al. 2010; Hassan et al. 2012; Carneiro et al. 2013; Osborn et al. 2014; Leng and Yu 2016), superhydrophobic (Nascimento et al. 2012; Arabzadeh et al. 2016a), self-cleaning (Nascimento et al. 2012; Carneiro et al. 2013), deicing/anti-ice (Liu et al. 2014; Aydin et al. 2015; Ma et al. 2016), self-healing (Agzenai et al. 2015; Hou et al. 2015; Tabakovic and Schlangen 2015; Lv et al. 2017; Pamulapati et al. 2017), thermochromic (Cardoso 2012; Hu et al. 2015; Zhang et al. 2018), and Latent Heat Thermal Energy Storage (LHTS) (Guan 2011; MeiZhu et al. 2011; Ma et al. 2014; Manning et al. 2015) are being investigated in road pavements. They intend to contribute positively by improving environmental, safety, and economic issues (reducing costs).

Heterogeneous semiconductor-mediated photocatalysis attracts significant interest due to its ability to efficiently convert ultraviolet (UV) light from solar radiation into chemical energy that can photodegrade harmful air pollutants. Due to the huge surface area of photocatalytic asphalt pavements and their proximity to car exhaust gases, they are cited as promising surfaces, with growing interest in the literature, for reducing the concentration of atmospheric pollutants SO_2 and NO_x (Cao et al. 2017; Ma et al. 2021; Segundo et al. 2021). In addition, some semiconductors act as catalysts when exposed to the action of UV radiation, promoting the photodecomposition of organic molecules adsorbed to the surface, such as oils and greases, cleaning it and mitigating the reduction of friction caused by these compounds, reducing the number of road accidents (Carneiro et al. 2013).

Several functionalization methods of asphalt mixtures for photocatalytic purposes are reported in the literature, namely asphalt binder modification, bulk incorporation, spreading, and spray coating, which is the most important. The spray coating is a surface treatment consisting of the deposition of particles dispersed into a solvent and spread with a paint gun. For the evaluation of this functionalization process, there are several methods; in which the most important ones are the gas degradation, using pollutants such as NO_x and SO_2, and the utilization of a dye as a model of pollutant (Segundo et al. 2019).

Asphalt pavement friction at safe levels is one of the primary concerns of Transportation Engineering. The presence of water, ice, and snow on the surface significantly decreases friction, negatively contributing to accidents' frequency and gravity (Baheri et al. 2021; Dalhat 2021; Lee and Kim 2021). Thus, the water, ice, and snow must be rapidly removed from the pavement's surface. An alternative to that is providing the superhydrophobic capability to the pavement surface with the application of particles, such as TiO_2 (Wu, C.; Li, L.;Wang, W.; Gu, Z.; Li, H.; Lin, X.;Wang 2021), and PTFE (Arabzadeh et al. 2016a), usually by spray coating (Arabzadeh et al. 2016b; Peng et al. 2018; Segundo et al. 2021). It is achieved when its water contact angle is higher than 150º (Arabzadeh et al. 2016b; Lee and Kim 2021).

The main objective of this research is to functionalize an asphalt mixture using micro-PTFE and nano-TiO_2 to provide it with photocatalytic, superhydrophobic, and self-cleaning properties. This smart material will be evaluated concerning wettability, photocatalysis, and chemical and morphological properties to ensure these functions are achieved.

Materials and Methods

Asphalt mixture

The asphalt mixture selected for the functionalization process was an AC 10, designated by R. The grading is composed of 68% of 4/10 and 28% of 0/4 aggregate fractions, 4% of filler., Its main volumetric properties are maximum bulk density of 2.428 g/cm^3, bulk density of 2.305 g/cm^3, and air voids of 5.1% and 5.5% of asphalt binder content.

Particles characteristics

The particles used in the functionalization process were nano-TiO_2 and micro-PTFE. The characteristics of these particles were checked through Fourier Transform Infrared Spectroscopy (FTIR) to analyse the chemical composition and the presence of chemical bonds (Fig. 1), Scanning Electron Microscopy (SEM) to analyse their surfaces (homogenization, dispersion, and particle size), and Energy Dispersive Spectroscopy (EDS) for chemical element analysis (Figs. 2 and 3).

Regarding the FTIR, for TiO_2, which is a simple structure of Ti and O, note the strong bands attributed to a stretching vibration of Ti–O bound (near to 401 cm-1). Also, two other bands are observed, one at 3309 cm−1, corresponding to the stretching vibration of the hydroxyl group O-H of the TiO_2 and another around 1643 cm−1, corresponding to bending modes of water Ti-OH (León et al. 2017; Rocha Segundo et al. 2018). For PTFE, which is composed of a chemical structure of the polymer macromolecules of (-CF2-)n, symmetric and asymmetric stretching vibrations of CF2 are observed at 1141 and 1203 cm-1. The peaks at 501-632 cm−1 are ascribed to CF2 rocking, wagging, and bending vibrations (oscillations of the pendulum and the deformation CF2-groups) (Fazullin et al. 2015; Wang et al. 2018; Piwowarczyk et al. 2019).

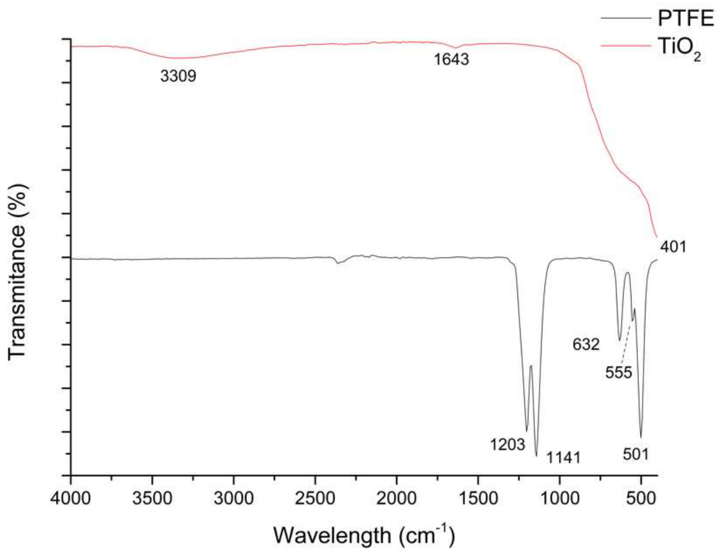

Figure 1. FTIR results of the particles used in this research

For SEM, the particle size of TiO_2 and PTFE was about 25 nm and 260 nm, respectively. Concerning EDS, the results indicate peaks of Ti and O for TiO_2 and C and F for PTFE, being in accordance with FTIR.

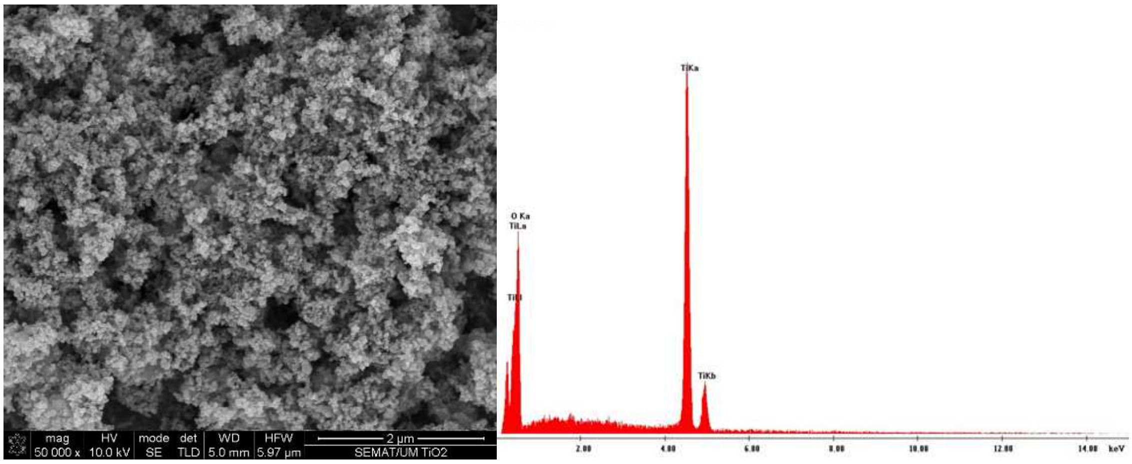

Figure 2. SEM and EDS results of the nano-TiO_2

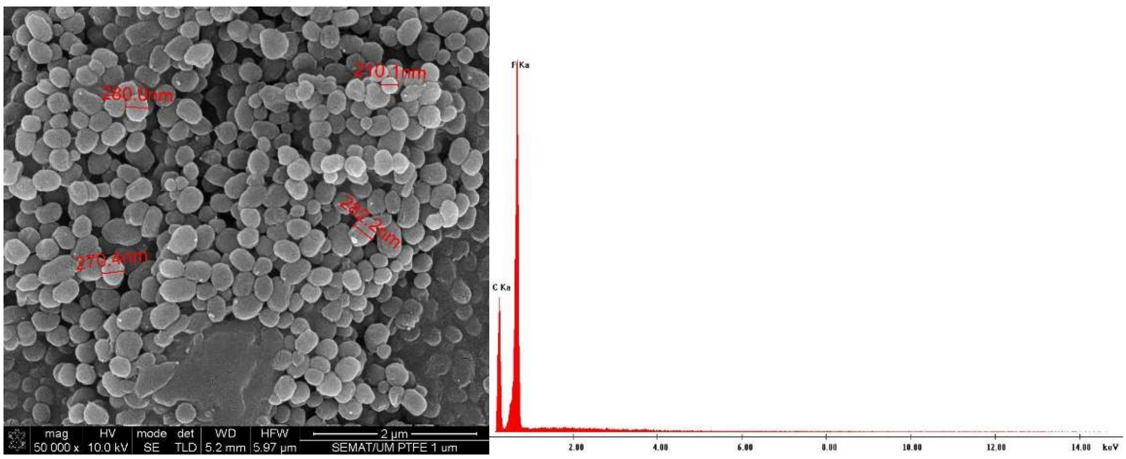

Figure 3. SEM and EDS results of the micro-PTFE

Sampling

The asphalt samples prepared for testing were extracted from slabs compacted in the laboratory, later cut with the dimension of 25 x 25 x 15 mm^3.

Functionalization procedure

For the functionalization process, two successive spraying coatings were carried out: i) the first one with a diluted epoxy resin (1:1 butyl acetate and resin) and the second one, immediately after the first one, with an alcoholic solution with nano-TiO_2 (4 g/L) and micro-PTFE (4 g/L), previously studied as the best solution (BS) (Segundo et al. 2022). The epoxy resin with two components was selected, as it is usually used in road pavements. This material was already used as a binder in the spreading method (Wang et al. 2016) and spraying coating method for the functionalization process (Arabzadeh et al. 2016b).

Analysis procedure

To analyze the photocatalytic efficiency, a dye (Rhodamine B - RhB) was used as a pollutant model, and its degradation was evaluated under solar simulation irradiation (Madhukar et al. 2016; Zhang et al. 2016). The cut asphalt samples were immersed in a 30 mL RhB aqueous solution with a concentration of 5 ppm. They were placed inside a box, 25 cm below a lamp

(11 W/m^2 of power intensity). The samples were kept for 3 h and 8 h under dark and light conditions, respectively. To quantify the efficiency, the maximum absorption of the dye was observed over time. Using Equation 1, the photocatalytic efficiency was calculated (Carneiro et al. 2013).

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

Where Φ is the photocatalytic efficiency, A0 and A represent respectively the RhB maximum absorbance for time 0 and "t" hour after irradiation.

To analyze the wettability, the samples were submitted to the Water Contact Angle test (WCA) (Arabzadeh et al. 2016a; Rocha Segundo et al. 2021). Three 5 µL water drop readings were performed in 2 samples for 2 minutes at room temperature and relative humidity.

Also, a SEM image and an EDS spectrum of the surface of the functionalized asphalt mixture were obtained to evaluate the particles' distribution and fixation.

Results and Discussions

The results of the photocatalytic efficiency are presented in Fig. 4 for samples with the epoxy coating (R-0.25g) and both epoxy and BS spraying coating (R-0.25g-BS). The efficiency of the sample with the BS coating was higher, achieving 43%.

Fig. 5 shows the results of the WCA for the same samples. The results indicate a much higher WCA for the sample with the BS coating (WCA > 150°), achieving the superhydrophobic capability.

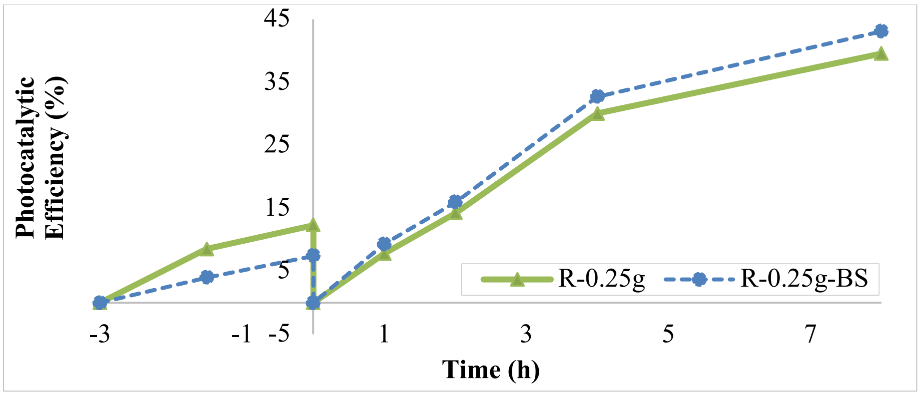

Figure 4. Photocatalytic efficiency results

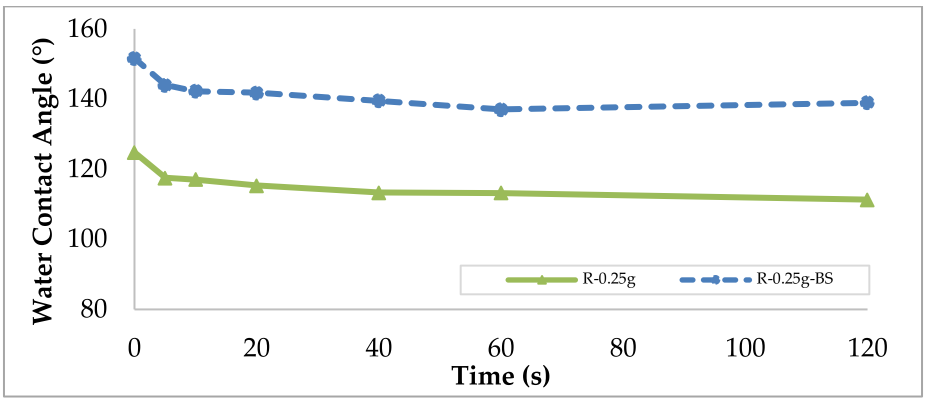

Figure 5. WCA results

The results of SEM of the functionalized asphalt mixture are shown in Fig. 6. It can be seen that the particles are dispersed on the resin, but some of them sank into the adhesive layer. On the one hand, this may improve the fixation of the particles. On the other hand, it may decrease the efficiency of the surface treatment since the particles are not exactly over the surface, reducing the availability of the particles for the irradiation, the contact with water (to repel it), and the contact with the pollutant (to photodegrade it).

The sinking effect of the particles in the resin layer can be avoided by using a more diluted resin or by reducing the mass of this layer to the lowest possible, as long as the immobilization of the particles is still satisfactorily guaranteed.

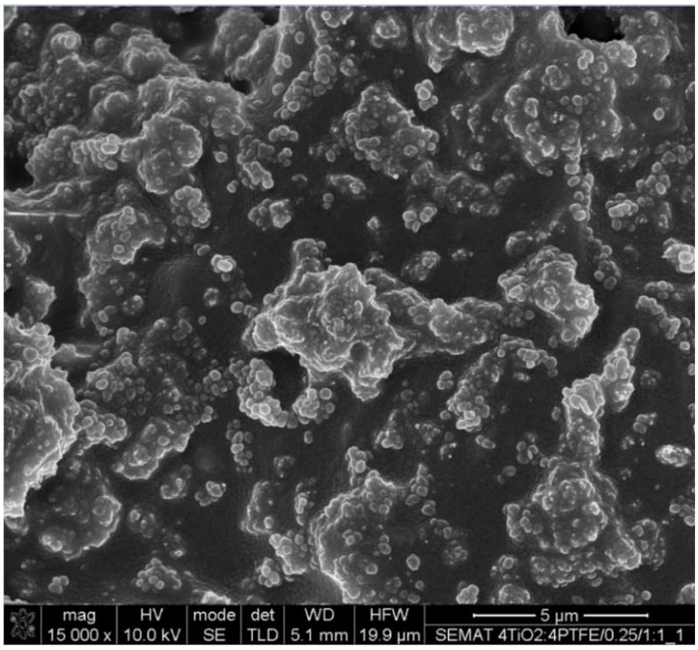

Figure 6. FTIR results of the particles used in this research

The results of the EDS are shown in Fig 7. It can be seen that C, F, Ti, and O are presented in the spectrum, indicating the existence of the particles TiO_2 and PTFE on this surface treatment. Other peaks are present, namely F, Na, Al, Si, K, S, and Ca, which probably are due to the resin or even to the asphalt mixture composition.

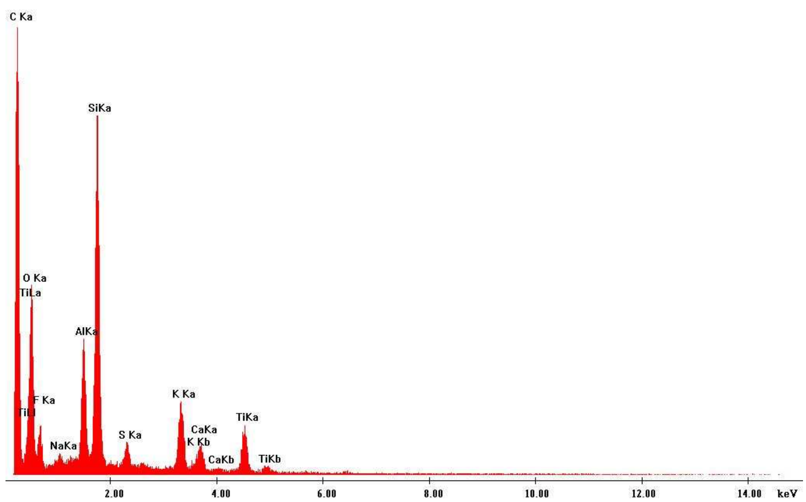

Figure 7. EDS results of the particles used in this research

Conclusions

The main objective of this research was to provide photocatalytic, superhydrophobic, and self-cleaning properties to an asphalt mixture using micro-PTFE and nano-TiO_2 by spraying coating. The main conclusions are that the new capabilities were achieved using two successive spraying coatings: the first one with an adhesive coating and the second one with a particle's solution.

The performance assessment considered the photocatalytic efficiency, water contact angle, SEM, and EDS tests. The SEM showed that the particles are fixed over the surface of the asphalt mixture, but the sinking of some particles in the resin can decrease the efficiency. Thus, changes in the amount of resin (adhesive coating), like its reduction, would be beneficial.

Overall, the achievements of this multidisciplinary research provide social and environmental benefits and contribute to the large-scale application of nanomaterials in the field of Civil Engineering, specifically to asphalt mixtures. Moreover, the surface characteristics of the asphalt pavements can be evaluated by essential characteristics such as friction, texture, noise, and enhanced physicochemical characteristics such as wettability and photocatalysis.

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References

Agzenai Y, Pozuelo J, Sanz J, Perez I, Baselga J (2015) Advanced self-healing asphalt composites in the pavement performance field: mechanisms at the nano level and new repairing methodologies. Recent Pat Nanotechnol 9(1):43–50. https://doi.org/10.2174/1872208309666141205125017

Arabzadeh A, Ceylan H, Kim S, Gopalakrishnan K, Sassani A (2016a) Superhydrophobic Coatings on Asphalt Concrete Surfaces. Transp Res Rec J Transp Res Board 2551(April):10–17. https://doi.org/10.3141/2551-02

Arabzadeh A, Ceylan H, Kim S, Gopalakrishnan K, Sassani A (2016b) Superhydrophobic coatings on asphalt concrete surfaces: Toward smart solutions for winter pavement maintenance. Transp Res Rec 2551(June):10–17. https://doi.org/10.3141/2551-02

Aydin D, Kizilel R, Caniaz RO, Kizilel S (2015) Gelation-Stabilized Functional Composite-Modified Bitumen for Anti-icing Purposes. https://doi.org/10.1021/acs.iecr.5b03028

Baheri FT, Poulikakos LD, Poulikakos D, Schutzius TM (2021) Ice adhesion behavior of heterogeneous bituminous surfaces. Cold Reg Sci Technol 192(April):103405. https://doi.org/10.1016/j.coldregions.2021.103405

Cao X, Yang X, Li H, Huang W, Liu X (2017) Investigation of Ce-TiO_2 photocatalyst and its application in asphalt- based specimens for NO degradation. Constr Build Mater 148:824–832. https://doi.org/10.1016/j.conbuildmat.2017.05.095

Cardoso PD (2012) Development of Microcapsule-Based Thermosensitive Coatings for Application to Road Pavements (translated from portuguese language). University of Minho

Carneiro JOO, Azevedo S, Teixeira V, Fernandes F, Freitas E, Silva H, Oliveira J (2013) Development of photocatalytic asphalt mixtures by the deposition and volumetric incorporation of TiO2 nanoparticles. Constr Build Mater 38:594–601. https://doi.org/10.1016/j.conbuildmat.2012.09.005

Dalhat MA (2021) Water resistance and characteristics of asphalt surfaces treated with micronized-recycled-polypropylene waste: Super-hydrophobicity. Constr Build Mater 285:122870. https://doi.org/10.1016/j.conbuildmat.2021.122870

Fazullin DD, Mavrin GV, Sokolov MP, Shaikhiev IG (2015) Infrared spectroscopic studies of the PTFE and nylon membranes modified polyaniline. Mod Appl Sci 9(1):242–249. https://doi.org/10.5539/mas.v9n1p242

Guan B (2011) Application of asphalt pavement with phase change materials to mitigate urban heat island effect. 2011 Int Symp Water Resour Environ Prot :2389–2392. https://doi.org/10.1109/ISWREP.2011.5893749

Hassan MM, Dylla H, Asadi S, Mohammad LN, Cooper S (2012) Laboratory Evaluation of Environmental Performance of Photocatalytic Titanium Dioxide Warm-Mix Asphalt Pavements. J Mater Civ Eng 24(5):599–605. https://doi.org/10.1061/(ASCE)MT.1943-5533.0000408

Hassan MM, Dylla H, Mohammad LN, Rupnow T (2010) Evaluation of the durability of titanium dioxide photocatalyst coating for concrete pavement. Constr Build Mater 24(8):1456–1461. https://doi.org/10.1016/j.conbuildmat.2010.01.009

Hou Y, Wang L, Pauli T, Sun W (2015) Investigation of the Asphalt Self-Healing Mechanism Using a Phase-Field Model. J Mater Civ Eng 27(3):04014118. https://doi.org/10.1061/(ASCE)MT.1943-5533.0001047

Hu J, Asce SM, Yu XB, Asce M (2015) Reflectance Spectra of Thermochromic Asphalt Binder: Characterization and Optical Mixing Model. J Mater Civ Eng 28(2):1–10. https://doi.org/10.1061/(ASCE)MT.1943-5533.0001387.

Lee E, Kim DH (2021) Simple fabrication of asphalt-based superhydrophobic surface with controllable wetting transition from Cassie-Baxter to Wenzel wetting state. Colloids Surfaces A Physicochem Eng Asp 625(March):126927. https://doi.org/10.1016/j.colsurfa.2021.126927

Leng Z, Yu H (2016) Novel method of coating titanium dioxide on to asphalt mixture based on the breath figure process for air-purifying purpose. J Mater Civ Eng 28(5):1–7. https://doi.org/10.1061/(ASCE)MT.1943-5533.0001478

León A, Reuquen P, Garín C, Segura R, Vargas P, Zapata P, Orihuela PA (2017) FTIR and raman characterization of TiO2 nanoparticles coated with polyethylene glycol as carrier for 2-methoxyestradiol. Appl Sci 7(1):1–9. https://doi.org/10.3390/app7010049

Liu Z, Xing M, Chen S, He R, Cong P (2014) Influence of the chloride-based anti-freeze filler on the properties of asphalt mixtures. Constr Build Mater 51:133–140. https://doi.org/10.1016/j.conbuildmat.2013.09.057

Lv Q, Huang W, Xiao F (2017) Laboratory evaluation of self-healing properties of various modified asphalt. Constr Build Mater 136:192–201. https://doi.org/10.1016/j.conbuildmat.2017.01.045

Ma B, Si W, Ren J, Wang HN, Liu FW, Li J (2014) Exploration of road temperature-adjustment material in asphalt mixture. Road Mater Pavement Des 15(3):659–673. https://doi.org/10.1080/14680629.2014.885462

Ma T, Geng L, Ding X, Zhang D, Huang X (2016) Experimental study of deicing asphalt mixture with anti-icing additives. Constr Build Mater 127:653–662. https://doi.org/10.1016/j.conbuildmat.2016.10.018

Ma Y, Li L, Wang H, Wang W, Zheng K (2021) Laboratory Study on Performance Evaluation and Automobile Exhaust Degradation of Nano-TiO2Particles-Modified Asphalt Materials. Adv Mater Sci Eng 2021. https://doi.org/10.1155/2021/5574013

Madhukar B, Wiener J, Militky J, Rwawiire S, Mishra R, Jacob KI, Wang Y, Kale BM, Wiener J, Militky J, Rwawiire S, Mishra R, Jacob KI, Wang Y (2016) Coating of cellulose-TiO_2 nanoparticles on cotton fabric for durable photocatalytic self-cleaning and stiffness. Carbohydr Polym 150:107–113. https://doi.org/10.1016/j.carbpol.2016.05.006

Manning BJ, Bender PR, Cote SA, Lewis RA, Sakulich AR, Mallick RB (2015) Assessing the feasibility of incorporating phase change material in hot mix asphalt. Sustain Cities Soc 19:11–16. https://doi.org/10.1016/j.scs.2015.06.005

MeiZhu C, Jing H, Wu S, Lu W, Xu G (2011) Optimization of Phase Change Materials Used in Asphalt Pavement to Prevent Rutting. Adv Mater Res 219–220(May):1375–1378. https://doi.org/10.4028/www.scientific.net/AMR.219-220.1375

Nascimento JHO, Pereira P, Freitas E, Fernandes F (2012) Development and characterization of a superhydrophobic and anti-ice asphaltic nanostructured material for road pavements. In: 7th International Conference on Maintenance and Rehabilitation of Pavements and Technological Control. At Auckland, New Zealand

Osborn D, Hassan M, Asadi S, White John R (2014) Durability Quantification of TiO2 Surface Coating on Concrete and Asphalt Pavements. J. Mater. Civ. Eng. 26:331–337

Pamulapati Y, Elseifi MA, Cooper SB, Mohammad LN, Elbagalati O (2017) Evaluation of self-healing of asphalt concrete through induction heating and metallic fibers. Constr Build Mater 146:66–75. https://doi.org/10.1016/j.conbuildmat.2017.04.064

Peng C, Zhang H, You Z, Xu F, Jiang G, Lv S, Zhang R (2018) Preparation and anti-icing properties of a superhydrophobic silicone coating on asphalt mixture. Constr Build Mater 189:227–235. https://doi.org/10.1016/j.conbuildmat.2018.08.211

Piwowarczyk J, Jedrzejewski R, Moszyński D, Kwiatkowski K, Niemczyk A, Baranowska J (2019) XPS and FTIR studies of polytetrafluoroethylene thin films obtained by physical methods. Polymers (Basel) 11(10):1–13. https://doi.org/10.3390/polym11101629

Rocha Segundo I, Freitas E, Branco VTFC, Landi S, Costa MF, Carneiro JO (2021) Review and analysis of advances in functionalized, smart, and multifunctional asphalt mixtures. Renew Sustain Energy Rev 151(June 2020):111552. https://doi.org/10.1016/j.rser.2021.111552

Rocha Segundo IG da IGD, Dias EALEAL, Fernandes FDPFDP, Freitas EF de EFD, Costa MFMF, Carneiro JOJOJO (2018) Photocatalytic asphalt pavement: the physicochemical and rheological impact of TiO_2 nano/microparticles and ZnO microparticles onto the bitumen. Road Mater Pavement Des. https://doi.org/10.1080/14680629.2018.1453371

Segundo IR, Freitas E, Branco VTFC, Landi S, Costa MF, Carneiro JO (2021) Review and analysis of advances in functionalized, smart, and multifunctional asphalt mixtures. Renew Sustain Energy Rev 151(June 2020):111552. https://doi.org/10.1016/j.rser.2021.111552

Segundo IR, Freitas E, Landi S, Costa MFM, Carneiro JO (2019) Smart, photocatalytic and self-cleaning asphalt mixtures: A literature review. Coatings 9(11). https://doi.org/10.3390/coatings9110696

Segundo IR, Zahabizadeh B, Landi S, Lima O, Afonso C, Borinelli J, Freitas E, Cunha VMCF, Teixeira V, Costa MFM, Carneiro JO (2022) Functionalization of Smart Recycled Asphalt Mixtures: A Sustainability Scientific and Pedagogical Approach. Sustain. 14

Tabakovic A, Schlangen E (2015) Self-Healing Technology for Asphalt Pavements. Adv Polym Sci. https://doi.org/10.1007/12

Wang D, Leng Z, Hüben M, Oeser M, Steinauer B, H??ben M, Oeser M, Steinauer B (2016) Photocatalytic pavements with epoxy-bonded TiO2-containing spreading material. Constr Build Mater 107:44–51. https://doi.org/10.1016/j.conbuildmat.2015.12.164

Wang H, Wen Y, Peng H, Zheng C, Li Y, Wang S, Sun S, Xie X, Zhou X (2018) Grafting polytetrafluoroethylene micropowder via in situ electron beam irradiation-induced polymerization. Polymers (Basel) 10(5). https://doi.org/10.3390/polym10050503

Wu, C.; Li, L.;Wang, W.; Gu, Z.; Li, H.; Lin, X.;Wang H (2021) Coating on Asphalt Pavement. Nanomaterials 11:1–19

Zhang H, Chen Z, Xu G, Shi C (2018) Physical, rheological and chemical characterization of aging behaviors of thermochromic asphalt binder. Fuel 211(September 2017):850–858. https://doi.org/10.1016/j.fuel.2017.09.111

Zhang W, Xiao X, Zeng X, Li Y, Zheng L, Wan C (2016) Enhanced photocatalytic activity of TiO_2 nanoparticles using SnS_2/RGO hybrid as co-catalyst: DFT study and photocatalytic mechanism. J Alloys Compd 685:774–783. https://doi.org/10.1016/j.jallcom.2016.06.199