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Photocatalytic asphalt pavement: the physicochemical and rheological impact of TiO_2 nano/microparticles and ZnO microparticles onto the bitumen

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A cost-effective solution to provide asphalt pavements with the photocatalytic property was addressed for the first time, based on the combination of low percentages of two semi-conductors, TiO_2 and ZnO. Two photocatalytic techniques – spray deposition and bitumen modification – were used. With the former, the chemical properties were evaluated by FTIR after spraying the bitumen samples with two aqueous solutions, one with acid PH and another alkaline, of nano-TiO_2. The solution with less chemical impact was the alkaline one. With the latter, Penetration, Softening Point, Mass Loss, Dynamic Viscosity, Complex moduli and Performance Grade, after the modification by TiO_2 nano/microparticles and ZnO microparticles, were analysed with two levels of ageing produced by the RTFOT. TiO_2 nano/microparticles and ZnO microparticles conducted to softer bitumens and better results of short-term ageing resistance and did not cause any deterioration to the bitumen before or after either short- or long-term ageing.

Keywords: functionalisation; photocatalysis; bitumen modification; nanomaterials; TiO_2; ZnO

Introduction

NO_x (NO and NO_2) and volatile organic compounds (VOC) are the main harmful gases to human health, emitted by vehicles (de Melo & Trichês, 2012; de Melo & Trichês, 2017; Dylla, Asadi, Hassan, & Mohammad, 2013; Hassan, Dylla, Asadi, Mohammad, & Cooper, 2012; Tang, Liu, Huang, & Cao, 2017). Some semiconductor materials, such as zinc oxide (ZnO), tungsten oxide (WO_3), titanium dioxide (TiO_2) and cerium oxide (CeO_2), act as catalysts in redox reactions that promote the photodegradation of pollutants, i.e. when these materials, in the presence of water (moisture) and oxygen, are irradiated with ultraviolet (UV) light emitted by the sun, reactive-free radicals have the ability to degrade organic pollutants transforming them into CO_2 and water, SO_2 into H_2SO_4 and NO_x into HNO_3, etc. (Agrios & Pichat, 2005; Fujishima & Honda, 1972; Hassan et al., 2012; Hassan, Dylla, Mohammad, & Rupnow, 2010; Liu, Wang, Zhang, & Fan, 2015; Zhao & Yang, 2003).

The road pavements, due to their large area and closeness to pollutants' sources, are potentially a good solution to help cleaning the atmosphere by the photocatalytic oxidation of pollutant

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agents. Taking into account that most of the road pavement surfaces are made of asphalt mixtures, further studying the impact and ageing of the application of that technique on physicochemical and rheological properties of asphalt became important. The contamination very frequently of oils and greases over the surface of asphalt pavements reduces expressively the friction (Harish, Avinash, & Harikeerthan, 2013). By the capability of degradation of these materials, it is possible to reduce accidents in oil spilled areas (Carneiro et al., 2013; Rocha Segundo et al., 2018).

Asphalt mixtures used in road pavements are produced with raw materials such as bitumen and aggregates. The bitumen represents a complex combination composed by hydrocarbons having small amounts of structurally analogous heterocyclic species and some heteroatoms like oxygen, sulphur and nitrogen besides small amounts of nickel, iron, vanadium, calcium and magnesium. Moreover, it is possible to divide bitumen into four groups (SARA fraction): saturates, aromatics, resins (composing together the maltenes) and asphaltenes (Lesueur, 2009; Traxler & Coombs, 1936).

The pavement deterioration is directly related to the ageing of the asphalt bitumen (the binder) that occurs due to the combined action of UV and oxidation in the presence of oxygen and high temperatures (Lamontagne, Dumas, Mouillet, & Kister, 2001). In the oxidation of bitumen by ageing, there is the loss of the volatile low molecular weight components (aromatics) which give rise to components with higher molecular weight and particularly the asphaltenes. There is an increase in bitumen stiffness and fragility due to the greater amount of asphaltenes. Short-term ageing of bitumen occurs in the mixture production process when it is mixed with aggregates at high temperatures. Long-term ageing occurs during the lifetime of the pavement (Gawel, Czechowski, & Kosno, 2016; Lesueur, Teixeira, Lázaro, Andaluz, & Ruiz, 2016). The higher oxidation occurs during the construction phase, changing the percentages of SARA fraction (Read & Whiteoak, 2003). The introduction of semiconductors into the asphalt mixtures, in order to provide a new capability (photocatalytic capability), can change the asphalt properties.

There are three techniques to produce photocatalytic asphalt mixtures: (i) surface spraying from an aqueous solution with semiconductors; (ii) incorporation in volume (as aggregate); (iii) bitumen modification. The first technique is the most efficient and uses less amounts of semiconductor materials, but it is important to verify the fixation (adhesion) of the semiconductors on the surface of the materials. The second one probably provides a best fixation but also needs the use of higher amounts of material comparing with the other ones. The last technique allows the analysis of the ageing impact of the semiconductors into the bitumen under the physical and rheological point of view (Carneiro et al., 2013; Hassan et al., 2012; Toro, Jobson, Haselbach, Shen, & Chung, 2016).

The photocatalytic efficiency achieved by using each different functionalisation technique depends on traffic wearing. At the beginning of pavements life, the spraying coating technique is expected to be more effective than the bitumen modification. After wearing, the bitumen modification might present better results for photocatalytic efficiency than the spraying coating technique. In fact, it is expected that for the case of using the spraying coating, most of the semiconductor nanoparticles will be mainly located and exposed at the bitumen surface and thus, they will be removed, over time, by traffic. On the other hand, for the bitumen modification method, the abrasion produced by continuous traffic will progressively expose the semiconductor nanoparticles that were enclosed by the bitumen. In both cases, the photocatalytic activity should increase with increasing percentages of semiconductors (Carneiro et al., 2013).

Following the results of Hassan, Mohammad, Asadi, Dylla, and Cooper (2012), the surface spraying coating technique by using an aqueous solution composed by 2% nano-TiO_2 in volume with a spraying rate of 0.05 L/m^2 increases in 11% the cost of the pavement. According to Hassan et al., a value of 2.25 \$/m^2 (value reported to 2012) was estimated for a photocatalytic coating obtained by surface spraying. However, it is expected that this value decreases significantly in the near future since the TiO_2 mass producing is growing all over the world (Hassan et al., 2012). The other referred modification techniques require the use of semiconductors applied to the entire asphalt mixture (i.e. the overall thickness) and not only over its surface. Thus, volume incorporation or bitumen modification by semiconductor materials leads to a much more expensive technical solution.

Previous studies indicate that modified bitumen with nanoparticles improves the adhesion between bitumen and aggregate because of the increase of specific surface area. The increase in nanoparticles percentage, from 1% to 7% of TiO_2 combined with 0.4 to 2.8% SiO_2, causes a decrease in penetration up to 14% and an increase in softening point up to 20% compared with the conventional bitumen (Shafabakhsh & Ani, 2015).

The incorporation from 2% to 6% of nano-TiO_2 or nano-ZnO decreases the penetration up to 29% and increase the softening point up to 11%, the ductility up to 34% and the flash point up to 4%. The increase in the percentage of nanoparticles leads to an increase in the bitumen viscosity (Nejad, Tanzadeh, Tanzadeh, & Hamedi, 2016). The bitumen modification with 5% of nano-TiO_2 or nano-ZnO leads to a stiffer bitumen, reducing 10% the penetration and increasing 24% the softening point, when compared to the original bitumen (Zhang, Su, Zhao, Zhang, & Zhang, 2016). Through the rheology test carried out using dynamic shear rheometer (DSR), the modified bitumen with 0.3% to 1.2% nano-TiO_2 led to higher complex moduli at 40–70°C.

UV light, which is necessary to initiate the photocatalysis, did not negatively affect the binder rheological properties of modified bitumen with 7% TiO_2 compared to a binder without nanoparticles (Hassan et al., 2012). Bitumens modified with 1% of organic expanded vermiculite (OEVMT) clays combined with 3% nano-TiO_2 and with 1% OEVMT and nano-ZnO provide a good thermal oxidation and UV ageing resistance compared with a conventional bitumen. The photo oxidation ageing resistance is given by the fact of the semiconductors can reflect and absorb the UV light (Chen, Zhang, Zhu, & Zhao, 2015).

The spraying coating was used to achieve the photocatalytic capability of asphalt mixtures including in real contexts (Asadi, Hassan, Nadiri, & Dylla, 2014; Bocci, Riderelli, Fava, & Bocci, 2016; Chen & Liu, 2010; Dylla et al., 2013; Liu et al., 2015; Osborn, Hassan, Asadi, & White John, 2014). By this method, it is possible to provide also superhydrophobic asphalt mixture surfaces (Rocha Segundo et al., 2018). The impact of the semiconductors' application was already evaluated by Carneiro et al. (2013) analysing the pH of the aqueous solution sprayed over the surface. An acid pH 5.5 solution containing nanoparticles applied by spraying onto the bitumen leads to a disappearance of the bee structure, associated with asphaltenes, analysed by atomic force microscopy (AFM); however, a basic pH 8 preserves it, indicating that the use of a solution with acidic pH is not feasible for the production of photocatalytic spraying technique (Carneiro et al., 2013). Also, Rocha Segundo et al. (2018) evaluated the impact of this technique by AFM and FTIR using an aqueous solution of nano-TiO_2, micro-ZnO and both semiconductors. They concluded that ZnO sprayed over the surface can affect the binder, but the other solutions including the combination did not cause any impact.

The literature review shows some investigation results of the asphalt modification with high percentages of micro/nanoparticles, but not with low percentages, that is, less than 1% by bitumen mass. It is expected that the use of a low particle percentage can increase the photocatalytic ability due to the low particle size and higher specific surface area, without causing negative effects in the bitumen properties.

In order to produce photocatalytic asphalt mixtures, it is important to analyse the impact of the semiconductors onto the asphalt binder. Thus, in this research, the chemical impact of two aqueous solutions laid down through the spraying technique with TiO_2 nanoparticles and the impact on physicochemical properties of modified bitumen with TiO_2 nano/microparticles and

ZnO microparticles, taking into account two levels of ageing, were analysed in order to assess if there is deterioration of the bitumen.

Materials

Bitumen

In this research, a bitumen, classified 35/50 by penetration grade, the most used bitumen in Portuguese road pavements, provided by Cepsa®, was used. The bitumen was characterised by: (i) Penetration of 38×10^{-1} mm (EN 1426/2015); (ii) Brookfield viscosity of 366 cP at 150°C (EN 13302/2010); (iii) Softening Point of 54°C (EN 1427/2015); (iv) 0.28% of mass loss, 50% retention penetration and 7°C softening point increase after Rolling Thin-film Ovens (RTFOT) (EN 12607/2014).

Semiconductor particles

In order to provide the photocatalytic property, TiO_2 nano/microparticles and ZnO microparticles were used since these semiconductor materials, when irradiated by light, are able to participate in oxidation/reduction chemical reactions to degrade dissimilar pollutants adsorbed at their surfaces. In addition, it can be pointed out that these semiconductor materials present low toxicity, low cost and high stability and availability, thus making them very important materials that can be used in large-scale applications (Diamanti, Ormellese, & Pedeferri, 2008; Ilican, Caglar, Caglar, & Demirci, 2008; Ni, Leung, Leung, & Sumathy, 2007).

The semiconductors nano-TiO_2 was purchased from Quimidroga, and micro-TiO_2 and micro-ZnO were purchased from Merck. Their main properties are: (i) nano-TiO_2: 80% anatase and 20% rutile crystalline phases, purity $> 99.5\%$, particle size of about 23–28 nm; (ii) micro-TiO_2: rutile; purity $> 99\%$, particle size less than 5 μm; (iii) micro-ZnO: wurtzite structure, purity $> 99\%$, particle size 45 μm.

Sample preparation

The preparation of the samples followed two methods: surface modification by spraying an aqueous solution of TiO_2 nanoparticles onto a film of bitumen; and, modification of TiO_2 nano/microparticles and ZnO microparticles into the bitumen (Figure 1).

In the first method, in order to evaluate the influence of the variation of the pH of the aqueous nanoparticles, two aqueous solutions of 4 g/L TiO_2 nanoparticles with different pH were prepared: acid pH (5); and, a basic pH (8). They were prepared using HCl and NaOH solutions to properly adjust acid and basic pH, respectively.

Bitumen was deposited in glass coverslips. After that, the samples were sprayed with the solutions using an atmospheric air compressor at a distance of about 20 cm, during 30 s, being the speed of the aqueous solution jet set at 100 mL/min, leading to coverage rates from about 5 to 12.5 mg/cm^2 according to the work of Carneiro et al. (2013) and Rocha Segundo et al. (2018). The control of the concentration of the solutions, the distance of application, time and the mass applied was very important to avoid high variability between the sprayed samples.

In the second method, the asphalt binders were modified with three distinct types of semiconductors: TiO_2 nanoparticles, TiO_2 microparticles and ZnO microparticles, which combination is presented in Table 1. The particles were incorporated into the bitumen at 160°C for 5 min in a low shear mixer. This process, commonly used in bitumen modification for the road pavements (Aydin, Kizilel, Caniaz, & Kizilel, 2015; Lu & Isacsson, 1997), is carried out through a

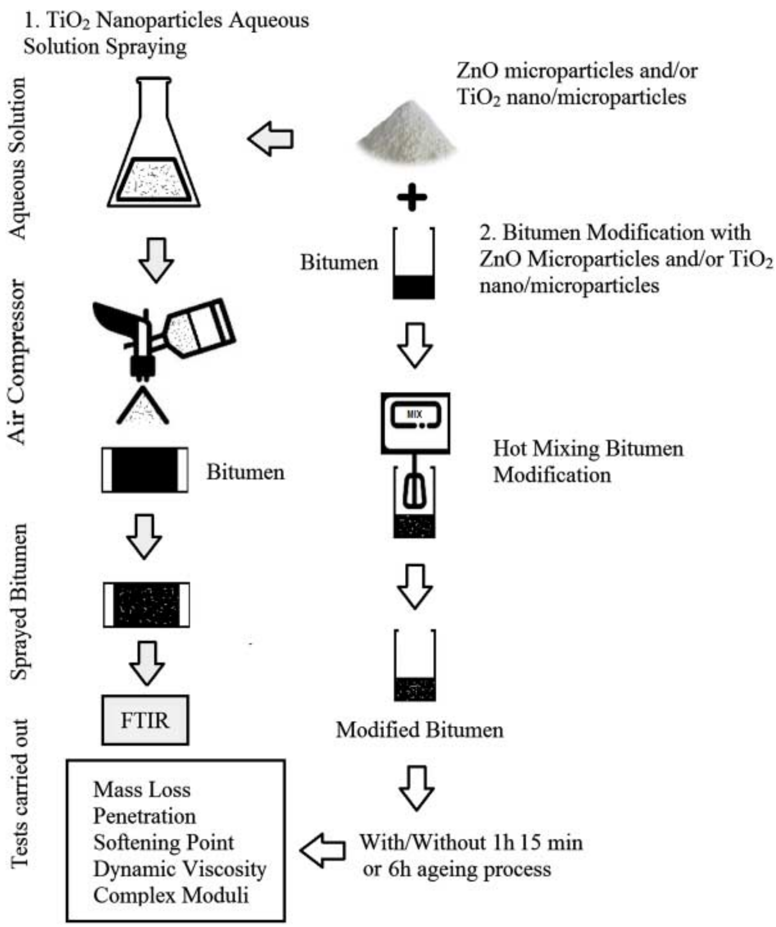

Figure 1. Preparation of samples and tests carried out.

Table 1. Semiconductors concentration by mass of bitumen.

Asphalt binder	TiO_2 nanoparticles (%)	TiO_2 microparticles (%)	ZnO microparticles (%)
L0	–	–	–
L1	0.06	–	–
L2	0.08	–	–
L3	0.10	–	–
L4	0.06	0.20	–
L5	0.08	0.20	–
L6	0.10	0.20	–
L7	0.06	0.20	0.20
L8	0.08	0.20	0.20
L9	0.10	0.20	0.20

continuous rotation using a shear rate of 200 rpm in order to ensure a homogeneous mix. In the process, the used time is appropriate to promote modification ensuring the mix homogeneity and at the same time, it is also short enough to avoid the bitumen ageing.

Characterisation methods and procedure

Initially, in order to evaluate the chemical impact of bitumen sprayed by the TiO_2 nanoparticles aqueous solution, Fourier Transform Infrared Spectroscopy (FTIR) was performed. The result gives details about the best pH to produce the solution used in the spray deposition technique. The FTIR spectrum was recorded on a system Avatar 360 FTIR, Nicolet, with a 4000–400 cm^{-1} spectral range, equipped with multi-bounce HATR and diffusion reflectance accessories. The spectrums are useful to compare the chemical impact of the different pH (acid and basic) TiO_2 nanoparticles aqueous solutions and the conventional bitumen without spraying.

The chemical structure of the bitumen was analysed by the calculation of structural indices, SI, from FTIR spectrum (Lamontagne et al., 2001). The SI was calculated by taking the ratio of the peak area of the identified band by the total area of the spectrum (Equation (1)). The variation between the functional group indices of the sprayed samples and the conventional bitumen ones will be presented in order to assess the chemical impact of the sprayed semiconductor material.

$$\mathrm{SI}_{\text{Functional group}} = \frac{\text{Peak area of the specific functional group}}{\Sigma\,\text{Area of FTIR spectrum}}, \tag{1}$$

In order to analyse the impact of bitumen modification by nano/microparticles before and after two different ageing levels, the following tests were performed: (i) Mass loss; (ii) Penetration; (iii) Ball softening point; (iv) Brookfield Dynamic Viscosity; (v) Rheology. For the Rolling Thin-film Oven Test (RTFOT) samples were aged during a period ranging between 1 h 15 min (standard EN 12607/2014) and 6 h. The time-extending RTFOT can be used to simulate the long-term ageing (Li, Ding, Zhang, & Zhang, 2016). The first three tests will be presented (Figures 3–5) comparing the modified bitumen by mass loss/penetration/softening point index calculated by the Equation (2).

$$Ii(\%) = \frac{\mu_{\mathrm{bi}} - \mu_{\mathrm{ci}}}{\mu_{\mathrm{ci}}} \times 100, \tag{2}$$

where Ii is the property index (%); i mass loss (m) or penetration (p) or softening point (s); μ_{bi} is mass loss, penetration or softening point result for the modified bitumen; μ_{ci} is mass loss, penetration or softening point result for the conventional bitumen (reference value of the property).

The mass loss was calculated after the ageing process due to the volatility of low-weight molecules. The bitumen hardness and the temperature susceptibility were measured by the penetration at 25°C and with the ring and ball softening point tests according to standards EN 1426/2015 and EN 1427/2015, respectively, in order to obtain their basic properties. Brookfield Dynamic Viscosity is used to determine the mixing and compaction temperatures (standard EN 13302/2010). This test was carried out at high temperatures (from 100°C to 180°C). The samples not aged and those aged 1 h 15 min by the RTFOT were submitted to these tests. After analysing the results, it was decided to test only part of the samples aged 6 h due to resources optimisation. In this case, the samples with the intermedium concentration of nano/microparticles (L2, L5 and L8) and the conventional bitumen were tested.

The rheology test was used to study materials with a viscoelastic behaviour. DSR evaluates the bitumen on two viscoelastic parameters that vary with temperature and loading time: the complex modulus G^*; and δ, the phase angle. This test was performed on bitumen samples with the intermedium concentration of nano/microparticles (L0, L2, L5 and L8) at 46°C, 52°C, 58°C, 64°C, 70°C, 76°C, 82°C and 88°C according to standard EN 13302/2012. With these results, the high-temperature bitumen's performance grade (PG) was calculated (standard AASHTO M 320-09).

Results

Chemical analysis of bitumens sprayed with TiO_2 nanoparticles aqueous solution by FTIR

In this work, FTIR was used to analyse the chemical composition of TiO_2 nanoparticles' modified bitumen test samples in glass coverslips. This method shows the chemical groups and bonds of the samples. In Figure 2, the major bands at 2916 and 2854 cm^{-1} peaks are associated with the asymmetric stretching C−H (CH_3 and CH_2) and the symmetric stretching C−H (CH_2) of hydrocarbon chain segments (Zhang et al., 2016). The peak at 1458 cm^{-1} results from the C−H bond's bending vibrations and the 1605 cm^{-1} peak corresponds to C=C bond in benzene ring and C−H bonds stretching vibration (Yao et al., 2013). The peaks at 725.14 and 1026 cm^{-1} correspond to rocking vibration (bending with torsion) characteristic of CH_2 bond and S=O bond, respectively (Masson, Pelletier, & Collins, 2001).

Through the spectrums (Figure 2), it is possible to observe that there are chemical bonds that remain despite the change of pH. However, the peak intensity associated with the different modes of vibration varies upon the change of pH values. Therefore, the material behaves differently as pH changes. Table 2 shows the SI and the index variations between sprayed bitumens and the original one. The variation for the identified peaks was up to 20% and 6% (in absolute values) for pH 5 and pH 8, respectively, evidencing that the use of pH 5 solution leads to a higher structural change in the original bitumen.

With a pH 8 solution, the vibration frequency is closer to that of the original bitumen. This aqueous solution with pH 8 should be used since its reaction with the bitumen does not damage the structure. As a result, the basic pH is better to produce aqueous solutions which incorporate TiO_2 nanoparticles making part of the spray deposition technique procedure. This conclusion is in accordance with the results of the literature, since by observing AFM images, the spraying of a TiO_2 basic pH solution preserves the bee-like structures of bitumens, whereas, the spraying of an acid pH solution leads to the disappearance of those structures.

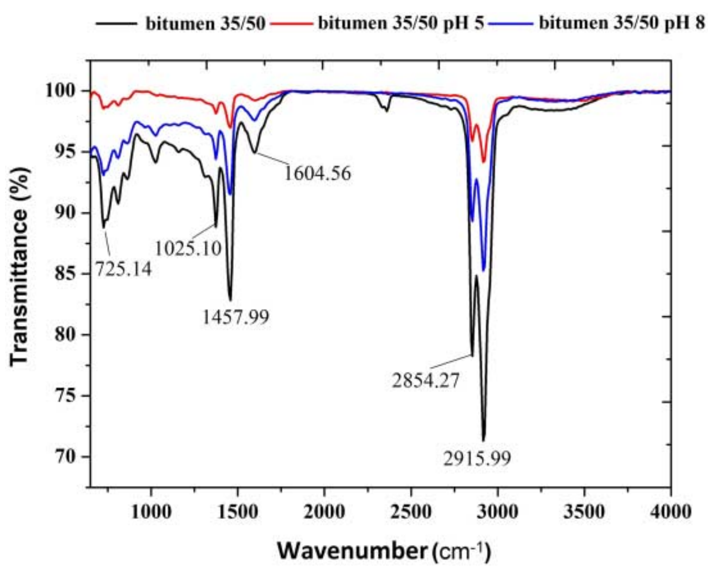

Figure 2. FTIR spectrum of modified bitumen with TiO_2 aqueous solution with acid and basic pH compared to the original bitumen.

Table 2. FTIR analysis in terms of structural indices (SI).

Peak wavenumber (cm^{-1})	Bitumen 35/50	Bitumen 35/50 pH 5		Bitumen 35/50 pH 8	
	SI	SI	Variation (%)	SI	Variation (%)
725.14	0.00875	0.01042	19	0.00889	2
1025.10	0.03997	0.03184	− 20	0.03831	− 4
1457.99	0.19451	0.21409	10	0.18352	− 6
1604.56	0.08262	0.09125	10	0.08457	2
2854.27	0.12713	0.12237	− 4	0.12011	− 6
2915.99	0.34928	0.40552	16	0.35168	1

Table 3. Properties of the bitumens before and after 1 h 15 min and 6 h RTFOT.

Asphalt binder	m 1 h 15 min RTFOT (%)	m 6 h RTFOT (%)	s (°C)	s 1 h 15 min RTFOT (°C)	s 6 h RTFOT (°C)	p (10^{-1} mm)	p 1 h 15 min RTFOT (10^{-1} mm)	p 6 h RTFOT (10^{-1} mm)
L0	0.28	0.29	54	61	78	38	19	13
L1	0.16	–	52	61	–	38	24	–
L2	0.15	0.29	55	61	78	42	26	13
L3	0.05	–	56	62	–	38	22	–
L4	0.2	–	55	62	–	40	24	–
L5	0.18	0.33	54	60	78	41	25	11
L6	0.18	–	53	62	–	40	24	–
L7	0.04	–	55	61	–	43	23	–
L8	0.17	0.34	55	62	78	38	24	13
L9	0.15	–	53	61	–	48	28	–

Physical and rheological impact of bitumen modification with nano/microparticles semiconductors

Table 3 shows the results of mass loss (*m*), softening point (*s*) and penetration (*p*) before and after 1 h 15 min and 6 h RTFOT. They will be discussed in the next sections using the indices *Im, Ip* and *Is* in order to analyse the mass loss, the penetration and the softening point, respectively.

Mass loss

As expected, after 1 h 15 min of the RTFOT test (Figure 3), all modified bitumens had an inferior mass loss compared to conventional bitumen. The negative mass loss index means that the modified bitumen had a lower mass loss than the conventional bitumen. The highest variations of the mass loss index (*Im*) were found on the samples L3 (82%), composed by 0.08% nano-TiO_2, and L7 (86%), composed by 0.06% nano-TiO_2, 0.2% micro-TiO_2 and 0.2% micro-ZnO, having the conventional bitumen as a reference. This result is in accordance with Hassan et al. (2012) that registered that 7% of nano-TiO_2 decreased the mass loss after RTFOT.

On the other hand, after a 6 h test, this behaviour changes and the mass loss of the modified bitumens have a mass loss index of up to 19.6% for L8 sample. Comparing the difference between mass losses after 1 h 15 min and after 6 h, the conventional bitumen had almost no change, but with the modified bitumens a major difference was registered. It can be concluded that the modified bitumen can resist to a short-term ageing better than the conventional one. At long-term ageing, the bitumens show a similar behaviour by 6 h RTFOT.

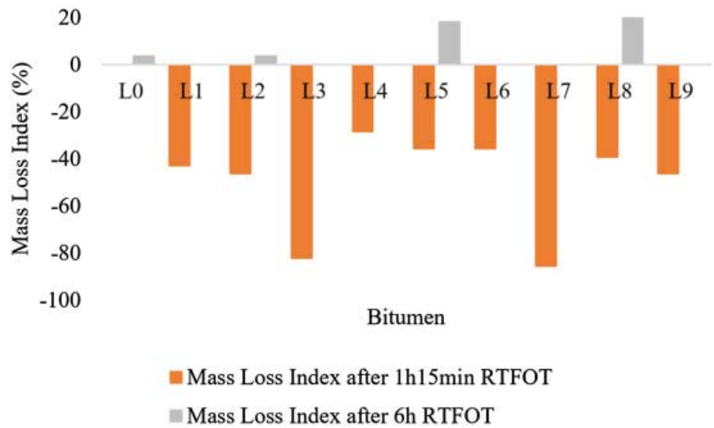

Figure 3. Loss mass index (*Im*) after 1 h 15 min and 6 h RTFOT.

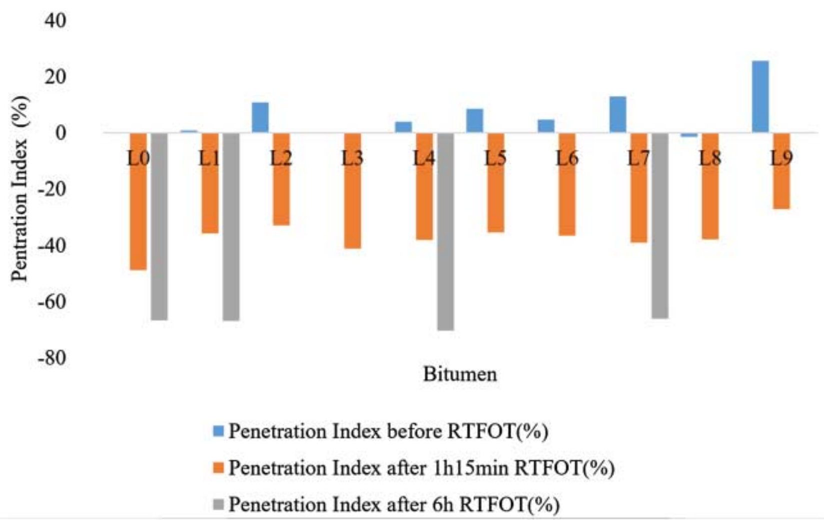

Figure 4. Penetration index (*Ip*) before RTFOT, after 1 h 15 min and 6 h.

Penetration

Figure 4 shows the variation of the bitumen penetration (penetration index *Ip*) for the samples with different combinations of semiconductors' nano/microparticles and level of ageing.

Before the RTFOT test, the modified bitumens show nearly the same penetration except for samples L2, L5, L7 and L9. The indices were 11%, 8%, 13% and 26% higher than for the conventional bitumen (L0), respectively, concluding that those samples were softer than the conventional one. Despite this fact, all the bitumens can be classified to 35/50 according to standard EN 1426/2015. With the use of at least 0.08% of semiconductor, it was possible to obtain softer bitumen. This conclusion is in accordance with the results of Nejad et al. (2016), but it does not accord with Zhang et al. (2016) and Shafabakhsh, Mirabdolazimi, & Sadeghnejad (2014). Probably, it was due to the lower content of semiconductor used in this paper.

After 1 h 15 min of ageing, the penetration index of all modified bitumens was lower than the conventional bitumen (L0) index. The lowest and highest indices were −49% (L0) and −27%

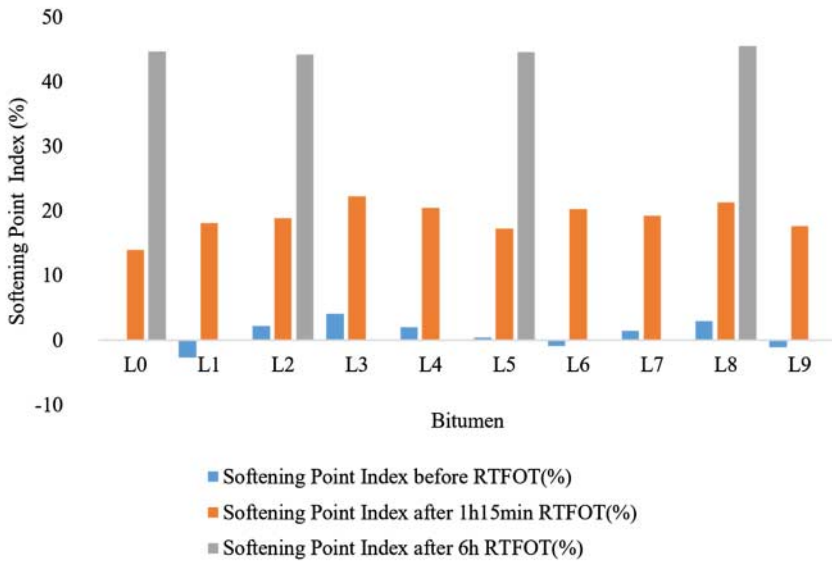

Figure 5. Softening point index (*Is*) before RTFOT, after 1 h 15 min and 6 h.

(L9: composed by 0.10% nano-TiO_2, 0.20% micro-TiO_2 and 0.20% micro-ZnO), respectively. In practical terms, in short time ageing, the modified bitumens are softer than conventional bitumen.

The comparison of samples with the same semiconductor percentage (difference of penetration indices after 1 h 15 min RTFOT and before RTFOT) shows higher differences to L0 (49%) while the presence of nano/microparticles on the bitumen leads to smaller differences. The L1-modified bitumen, with the smallest percentage of semiconductor, leads to the smallest difference (37%) and the L9-modified bitumen, with the biggest percentage of semiconductor, to the biggest one (53%).

In order to analyse the long-term ageing effect, the results of the RTFOT test carried out 6 h in L0, L2, L5 and L8 (bitumens with intermediate percentages of nano/microparticles) samples show similar values for the penetration index. For the same percentage of semiconductors, the differences before and after RTFOT are also similar, 67% on average. In the long-term ageing, the bitumens show a similar behaviour.

Softening point

Figure 5 shows the results of the variation of the softening point (softening point index *Is*) of the bitumen with the semiconductors' nano/microparticles. Before and after 1 h 15 min RTFOT, the softening point index is almost the same in average for all the samples: 1% and 19%, respectively. After ageing 6 h, the samples tested resulted in the same softening point, 78˚C, corresponding to an average softening point index of 45%. No significant variation of this characteristic of the bitumen with the addition of semiconductors' nano/microparticles analysed by softening point was found.

Brookfield dynamic viscosity

The dynamic viscosity of all modified bitumens is similar to the conventional bitumen (L0) viscosity, except for sample L7 (composed by 0.06% nano-TiO_2, 0.20% micro-TiO_2 and 0.20% micro-ZnO) which is somewhat higher for low temperatures (Figure 6). The same performance

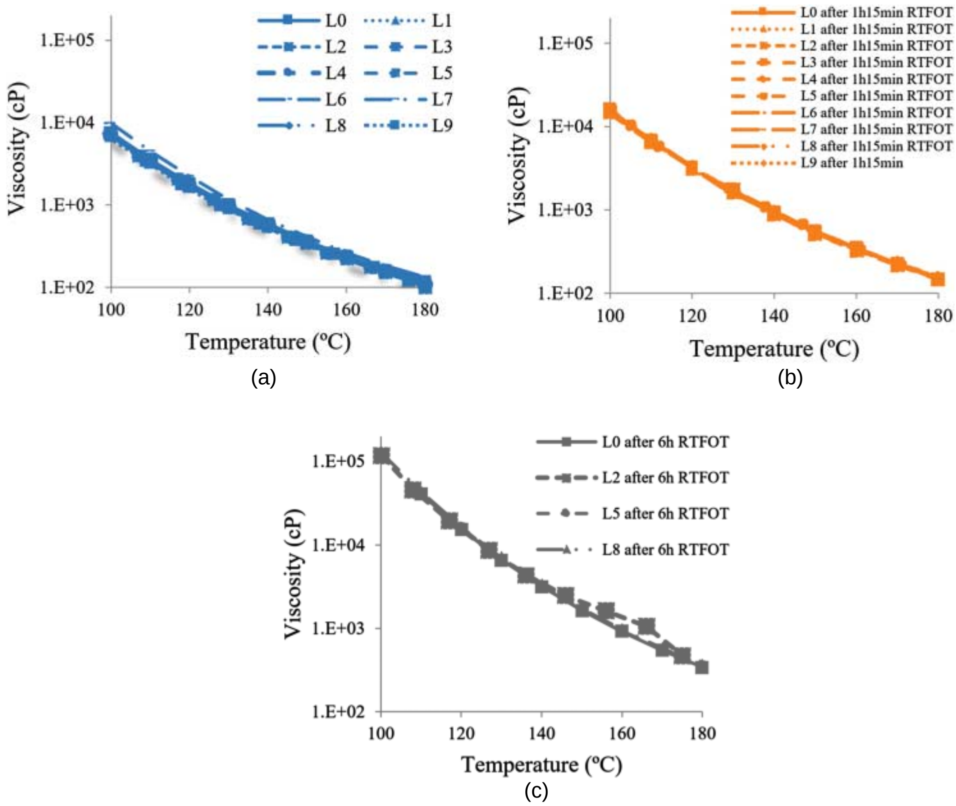

Figure 6. Dynamic viscosity of modified bitumen with nano/microparticles: (a) no ageing; (b) after 1 h 15 min RTFOT; (c) after 6 h RTFOT.

was found for the dynamic viscosity of the modified bitumen subjected to RTFOT. Also, for the samples subjected to 6 h RTFOT, there was no significant variation in this parameter. The viscosities are all similar except for the L2 sample where it can be seen that for temperatures between 150°C and 180°C, the viscosity is higher than the other samples. As can be seen in Figure 6, there are no significant changes to the viscosity of the samples tested.

Rheology

The Rheology results carried out with a DSR are shown in Figure 7. The temperature seems to affect rheology results. Before RTFOT, the complex modulus of the modified bitumen is lower than the conventional bitumen modulus at low temperatures. For high temperatures, they have the same value. Among the modified bitumens, L5 is closer to L0 (conventional bitumen). Thus, the largest difference of the complex modulus value occurs when comparing samples L2 (0.08% nano-TiO_2) and L0, with 33%. Regarding samples L5 (composed by 0.08% nano-TiO_2 and 0.20% micro-TiO_2) and L8 (composed by 0.08% nano-TiO_2, 0.20% micro-TiO_2 and 0.20% micro-ZnO), these values are 18% and 22%, respectively, lower than the conventional bitumen moduli. Unlike this research, stiffer asphalt binders analysed by rheology using these semiconductor materials were reported by Sadeghnejad & Shafabakhsh (2017) probably due to the high content of semiconductor.

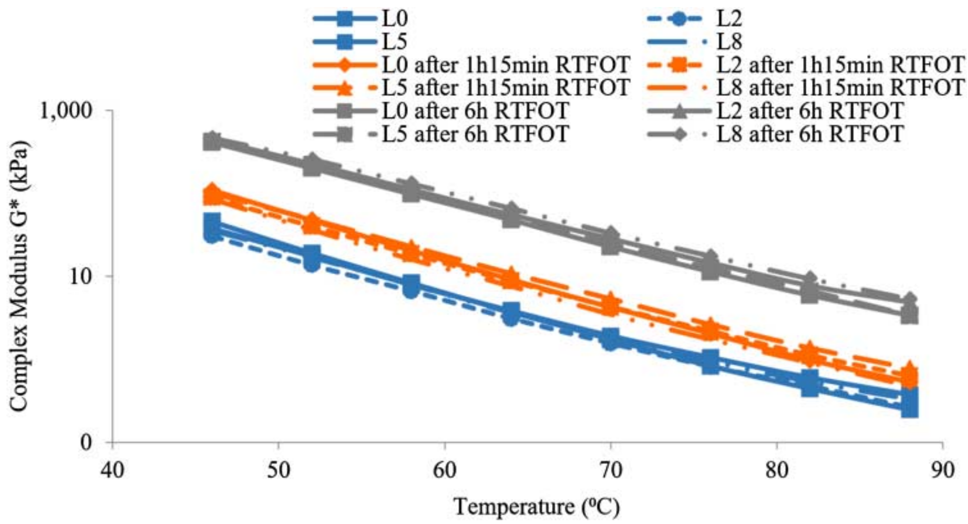

Figure 7. Complex moduli of modified bitumen with nano/microparticles.

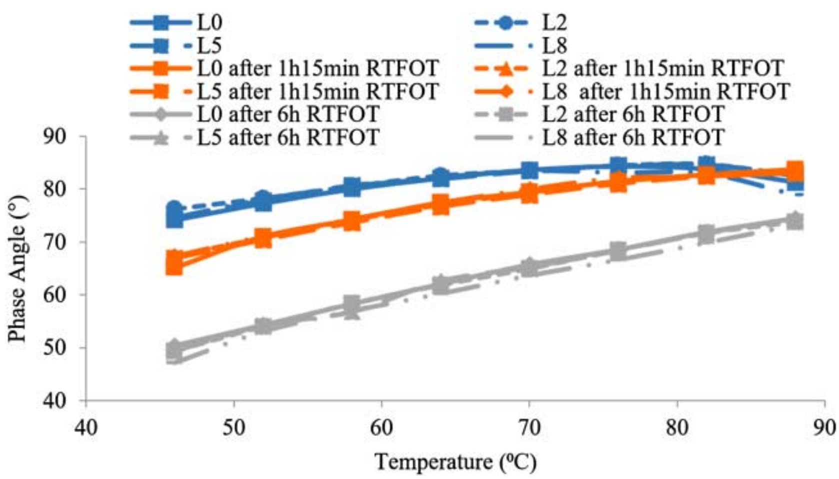

Figure 8. Phase angle of modified bitumen with nano/microparticles.

After 1 h 15 min RTFOT, the same performance as before ageing was observed. The complex modulus of the modified bitumen is lower than the conventional bitumen (L0) at lower temperatures. At these temperatures, the greatest difference relative to conventional bitumen complex modulus occurs for L8 sample (21%), followed by the L2 sample (18%) and L5 (8%). For higher temperatures, the modulus values are similar.

After 6 h RTFOT at low temperatures, the modified bitumens were slightly harder when compared with the conventional bitumen. At high temperatures, the bitumens have the same complex modulus.

Before RTFOT, the phase angles of the modified bitumens showed in Figure 8 are similar to the conventional bitumen. At lower temperatures, they have the same phase angle, except L2 which value is slightly higher. At high temperatures, the modified bitumens have a bigger phase

Table 4. Performance grade of the modified bitumens.

Bitumen	Temperature at which $G^*/\sin d = 1$ kPa before RTFOT (°C)	Temperature at which $G^*/\sin d = 2.2$ kPa after 1 h 15 min RTFOT (°C)
L0	70	70
L2	70	76
L5	76	76
L8	70	70

angle when compared with conventional bitumen values, except for sample L8. After the RTFOT procedure, the bitumens had the same phase angle.

Based on complex modulus and phase angle, bitumens have the same behaviour for the same level of ageing.

Performance grade

The PG of the bitumens was calculated with rheology results (Table 4). The PG of the modified and conventional bitumens was similar. They were slightly higher for L5 before ageing and after 1 h 15 min RTFOT, L2 increased slightly while the other remained as before. It can be concluded that intermediate concentrations of TiO_2 nano/microparticles led to an increase in PG before and after 1 h 15 min of RTFOT.

Conclusions

This study evaluated the physicochemical and rheological impact of adding TiO_2 nano/microparticles and ZnO microparticles in asphalt mixtures to produce photocatalytic bitumen mixtures by aqueous solution spraying or bitumen modification. In order to determine whether the modification of the bitumens with those particles could contribute negatively to their performance, before and after ageing, two application methods were used: a TiO_2 aqueous solution applied by spraying; and using the semiconductors as bitumen modifier. The following conclusions may be withdrawn:

- The pH of the aqueous solution has a significant effect on the bitumen physical integrity. Acidic solutions cause an impact on the bitumen. On the other hand, alkaline solutions while maintaining the integrity of the bitumen also generate a more stable spectrum by FTIR.
- The modified bitumens lead to smaller mass loss after 1 h 15 min RTFOT and almost no influence is registered when the ageing time is increased to 6 h. The bitumen penetration was not influenced before RTFOT, but it was higher for all modified bitumen after 1 h 15 min RTFOT. After 6 h RTFOT, the penetration was almost the same as after 1 h 15 min. There was a non-significant variation of the characteristics of the bitumen with the addition of particles in the softening point (before and after 1 h 15 min RTFOT and 6 h RTFOT). The empirical tests – mass loss, penetration and softening point – carried out on the modified bitumens showed a lower ageing in short terms, but in long terms, no changes were noticed.
- All modified bitumens had almost the same rotational viscosity by Brookfield and rheology properties compared to the conventional bitumen (L0) before and after 1 h 15 min and 6 h RTFOT, leading to the conclusion that the nanoparticles have practically no influence in these properties.

- On the rheological point of view, TiO_2 nano/microparticles and ZnO microparticles cause no deterioration into the bitumen before or after short- or long-term ageing. Modified bitumen had lower complex modulus than the conventional bitumen at low temperatures before and after 1 h 15 min RTFOT.

The main conclusion of this research work was to assure that photocatalytic asphalt pavements may be produced without physicochemical and rheological impacts into the bitumen. With the use of at least 0.08% of nano-TiO_2, it is possible to obtain softer bitumens and better results of short-term ageing resistance. The introduction of different types of semiconductors did not affect considerably the rheological properties of the bitumen. However, the combination of both semiconductors can promote changes in photocatalytic efficiency since the combined semiconductors would promote positive influence in their ability to absorb light energy in a more extended region of the electromagnetic spectrum, ranging from UV to visible region, thus enhancing the photocatalytic efficiency. It is expected that the UV ageing resistance will improve with the combination of both semiconductors.

The next step of this research is to analyse the bitumen after only exposure to UV light or combined to RTFOT through the pressure ageing vessel (PAV) test. Additionally, conventional tests such as fatigue, water sensitivity and permanent deformation after UV light ageing will be carried out in aged asphalt mixtures.

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