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RESEARCH PAPER

Rheological Evaluation of Asphalt Binder Modified with Nanoparticles of Titanium Dioxide

Paulo Germano Tavares Marinho Filho[1] · Alana Tamires Rodrigues dos Santos[1] · Lêda Christiane Lucena[1] · Eduardo Antonio Guimarães Tenório[1]

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Abstract

Premature cracks and permanent deformations are usual problems in Brazilian main road asphalt pavements. Researches intended to solve that problems have been developed with asphalt binder modified with polymers, fibre and recently nanoparticles. This article aims to study the incorporation of nanoparticles of titanium dioxide (TiO_2) on binder 55/75-E in percentages 0%, 3%, 4%, 5% of binder mass. The modified and pure binders were evaluated in two stages: first stage binders were analysed by Fourier transform infrared spectroscopy (FTIR), second stage consisted in physical and rheological tests: penetration, softening point, rotational viscosity, performance grade (PG); these tests were performed before and after short-term ageing procedure (RTFOT), multiple stress creep and recovery (MSCR) and linear amplitude sweep (LAS). Results show that binders with TiO_2 developed a high performance than the pure binder in high temperatures. This behaviour was verified through elevated stiffness and high softening point. TiO_2 addition promoted non-recoverable compliant reduction, suggesting a boost in the resistance to permanent deformation. Modified binders, also, demonstrated a delay on ageing that can be testified by ageing index and reduction in loss of mass.

Keywords Asphalt binder · Nanoparticles · Rheology · Titanium dioxide

1 Introduction

Cracks and premature permanents deformation are associated with asphalt binder performance. Modified binders may be a solution to avoid these problems and provide more safety and comfort to users, as well to lower maintenance budget for main roads. Modified binders are more resistant to permanent deformation, fatigue cracks and thermic variation. Therefore, these binders allowed a long useful life of pavement and reduction in operation and maintenance cost when compared to non-modified binders [1].

Yao et al. [2] and Li et al. [3] suggest that nanomaterial introduction in asphalt binder already modified for polymers is beneficial. According to the authors, nanomaterial promoted better interaction between polymers and asphalt matrix, as well, reduces polymers segregation and improve stability of modified asphalt binder.

Nanomaterials have been successfully used in many researches worldwide to improve engineering proprieties of asphalt binder [4–9]. Hamedi [9] evaluated and asphalt mixture of a binder 60–70 with aggregates coated with nano-Al_2O_3 and nano-Fe_2O_3. Authors performed a modified Lottman test in asphalt mixtures with and without nano-additives. Authors conclude that nano-additive improved asphalt mixture resistance to moisture. Shafabakhsh et al. [5] studies indicated the possibility of nano-titanium dioxide to improve asphalt binder resistance to fatigue, permanent deformations and oxidative ageing. Despite these studies, rheological behaviour of nano-

✉ Lêda Christiane Lucena
ledach@uol.com.br; leda.lucena@ufcg.edu.br

Paulo Germano Tavares Marinho Filho
marinho.paulo05@gmail.com

Alana Tamires Rodrigues dos Santos
s.alanarodrigues@gmail.com

Eduardo Antonio Guimarães Tenório
eduardo_agt123@hotmail.com

[1] Federal University of Campina Grande, Campina Grande, PB 58429-900, Brazil

titanium dioxide modified asphalt binders is still not fully understood.

Khattak et al. [10] studied incorporation of carbon nanofibres in asphalt binder. Authors found out evidence that modified binders got high resistance to rutting. Authors, also, highlighted difficulties in mix process, as well scalability and increasing in viscosity at mix and compaction temperature.

New studies identified rheological benefits such as increases in stiffness and decrease in phase angle after addition of nano-clay in asphalt binder [11, 12]. You et al. [6] studied nanoclay addition influence in asphalt binder. Authors verified that nanoclay improve mechanical proprieties, as well binder viscosity. Golestani et al. [4] studied nanoclay and styrene–butadiene–styrene (SBS) addition to asphalt binder. Authors concluded that nanoclay enhance viscosity and elastic parameters. Authors detected that nanoclay and SBS-modified binder is more resistant to moisture damage as well.

Zare-Shahabadi et al. [13] studied bentonite clay and organically bentonite clay addition to asphalt binder. Authors realize that bentonite modified asphalt binder had rutting resistance improved. Authors also detected that modified binders had lower creep stiffness. This fact suggests that bentonite clays improve cracking resistance in low temperature.

Zhang et al. [7] studied the influence of expanded vermiculite and nano-zinc oxide on physical, rheological and ageing proprieties of asphalt binder. Authors find out that vermiculite and nano-zinc oxide has been improved asphalt binder stability in high-temperature, as well boost binder resistance to oxidation and ageing. However, according authors contents of nano-zinc bigger than 4% have a negative influence.

Application of nanomaterial in binders pre-modified with polymers promotes better compatibility among asphalt matrix and polymers and bring improvements to the asphalt binder [4, 8, 14]. Zhang et al. [8] studied synergetic effect of vermiculite and nano-zinc oxide in styrene–butadiene–styrene modified asphalt binder. Authors concluded that vermiculite and nano-zinc oxide increased consistence and boost rheological and physical performance of SBS asphalt binder. Authors also performance FTIR spectroscopy test and verified that vermiculite and nano-zinc oxide avoided carbonyl formation in SBS binder during ageing.

Recently researches used titanium dioxide as binder modifier [5, 15, 16]. These researches suggest that TiO_2 promotes improvements in fatigue resistance, permanent deformation and oxidative ageing of binder. Zhang et al. [14] suggest that TiO_2 in association with other modifiers, as polymers, can enhance softening point and binder ductility. The elevated resistance of TiO_2 to chemical attacks, thermal wear, and ultraviolet degradation, associated with TiO_2 abundance makes this dioxide a potential modifier to asphalt binders.

Hassan et al. [17] studied ultra-fine powder TiO_2 incorporation in asphalt binder with a performance grade of 64/16. Authors analysed TiO_2 capability to remove air pollutants and its influence in rheological proprieties of binder. Authors concluded that TiO_2 can improve air quality and have no negative effects in physical proprieties. Hu et al. [18] studied nano-TiO_2 waterborne epoxy resin addition as seal and decomposer to exhaust material. Authors verified that nano-TiO_2 can degrade most pollutants from automobile exhaust, as well improve seal proprieties.

Shafabakhsh et al. [5] modified an asphalt binder 60/70 penetration grade with nano-TiO_2. Authors find out that the content of 5% of binder mass is the optimum content of TiO_2 to improve engineering proprieties of bitumen. Authors, also, concluded that TiO_2 can improve creep comportment and prevent vertical cracks. Tanzadeh et al. [19] also modified asphalt binder with nanoparticles of TiO_2 at the contents of 2%, 4% and 6%. Authors detected that TiO_2 improve fatigue life and flexural stiffness.

Researches showed above demonstrated that the use of nanomaterial and TiO_2 in asphalt binders allowed improvements in fatigue resistance, softening point, ductility, and material ageing. However, adequate use of TiO_2 as a successful modifier demands a rheological proprieties study of the binders as highlighted by Shafabakhsh et al. [5] and Zhang et al. [20].

Rheological analysis allows this article to evaluate with more accuracy nano-TiO_2 influence in binders pre-modified with polymers. Rheological analyses also can improve understanding about nano-TiO_2 interference in polymers behaviour when both additions are used as asphalt binder modifiers. Therefore, this article is dedicated to fulfilling a currently gap in the technical literature through the studying the rheological influence of TiO_2 incorporation to binders pre-modified with polymers.

2 Materials and Methods

This research used asphalt binder modified with polymers, styrene–butadiene–styrene (SBS) with penetration grade 55/75, denominated asphalt binder 55/75-E. Table 1 shows physical proprieties of asphalt binder.

Nanoparticles of TiO_2 were used as modifier agent. TiO_2 was analysed through tests of laser diffraction particle sizing, X-ray diffraction and efflorescence, differential thermal analysis (DTA) and thermal gravimetric analysis (TGA).

Table 1 Physical properties of asphalt binder 55/75—E

Tests	Methods	Unity	Specification	result
Penetration	ASTM D5 / D5M [21]	0.1 mm	45 to 70	56
Softening point	ASTM D36 / D36M [22]	°C	> 55	52
Rotational viscosity	ASTM D4402 / D4402M [23]			
at 135 °C, SP 21, 20 rpm		cP	< 3000	978
at 150 °C, SP 21, 50 rpm			< 2000	464
at 177 °C, SP 21, 100 rpm			< 1000	157
thermal susceptibility index	–			− 0.44
Elastic recovery at 25 °C	ASTM D6084 / D6084M [24]	%	> 75	82
mass variation	–	%	< 1	0.05
Incrementing of softening point	ASTM D36 / D36M [22]	°C	< 7	3.5
Original penetration percentage	ASTM D5 / D5M [22]	%	> 60	77

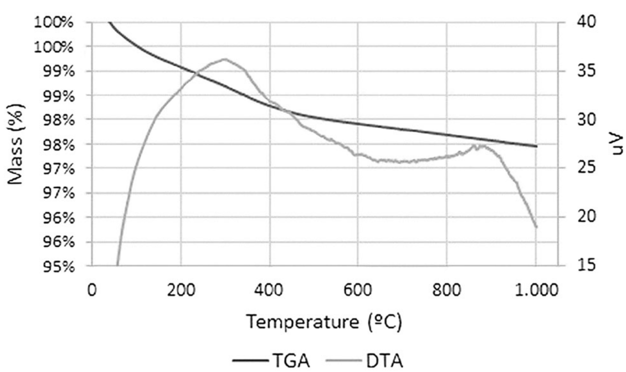

Fig. 1 Thermal differential and thermos-gravimetric analysis of TiO_2

DTA curve (Fig. 1) shows peaks at 300 °C and 900 °C. These events are exothermic and are linked to loss of mass of 2.5% observed in the TGA curve. All events occurred at temperatures higher than working temperature of asphalt pavement. Therefore, TiO_2 is not going to decompose when used as modifier.

X-ray diffraction (Fig. 2) shows crystalline structure of the TiO_2 and the presence of only TiO_2 peaks. X-ray efflorescence confirmed purity of the material by indicating 90.37% of TiO_2.

Diameter distribution of particles obtained by laser diffraction analyse is shown in Fig. 3. Effective diameter is in range of 130 nm classifying the material as nanomaterial.

2.1 Sample Preparation

Titanium dioxide was incorporated into asphalt binder on contents of 0%, 3%, 4% and 5% of binder mass. These contents were chosen based in Shafabakhsh et al. [5] study. Authors used contents of 1%, 3%, 5% and 7% of nano-TiO_2 in asphalt mixture. Authors concluded that 5% content was the optimum content to boost mechanical and consistence properties of asphalt mixture. Binder mix occurred through binder heating at 150 °C in a mechanical mixer that shakes binder at 2000 rpm for 90 min. The percentages of TiO_2 were added slowly during mixing process. Chemical analysis was conducted in asphalt binder after the incorporation of TiO_2.

2.2 Tests

Physical properties of modified binder were determined through penetration test [21], softening point test [25], rotational viscosity test using [26] and ageing—RTFOT [27].

Penetration test consists in measure the penetration depth of a standardized needle with 100 g in an asphalt binder sample during 5 s at 25 °C. Softening point test consists of raising the temperature, at a rate of 5 °C per minute, of a binder sample confined in a ring with a ball over it, when ball touch sample bottom temperature is noted as softening point temperature.

Rotational viscosity test was conducted with a viscosimeter Brookfield—DV II e DV III and a spindle 21, samples had 8 g and variation tolerance of 1% was used in each sample. The ageing procedure, RTFOT, was conducted in a rolling thin-film oven samples with 35 g and variation tolerance of 1%.

Rheological properties were analysed on DSR of series Discovery Hybrid Rheometer (DHR-1) by tests shown in Table 2.

Performance grade (PG) test was realized before and after RTFOT. Each PG analysis measures shear modulus (G^*) and sine of phase angle (δ) ratio, parameter $G^*/\sin(\delta)$. Parameter $G^*/\sin(\delta)$ must be below 1 kPa before RTFOT and below 2.2 kPa after RTFOT. Ageing index (AI) was measured by relation between $G^*/\sin(\delta)$ after and before

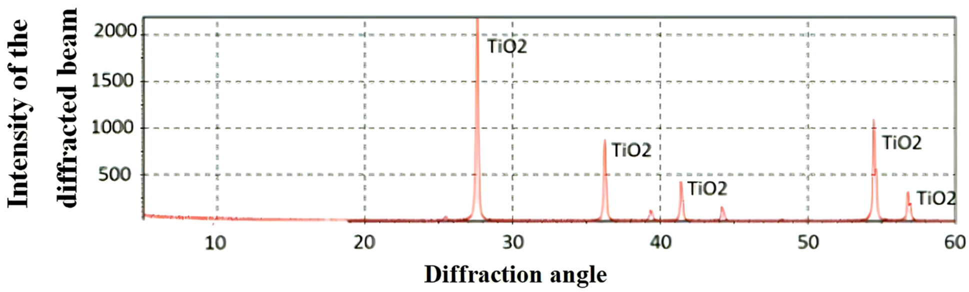

Fig. 2 X-Ray diffraction of TiO_2 particles

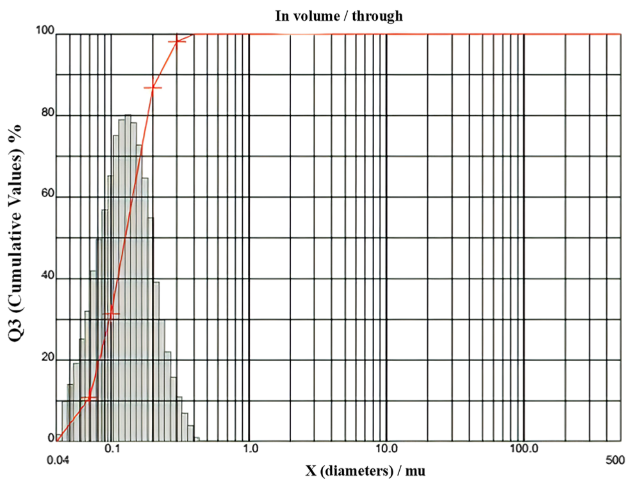

Fig. 3 Analysis of the TiO_2 particles diameter distribution by laser diffraction

Table 2 Tests for rheological characterization

Test	Standard	Sample dimensions (mm)	Variation tolerance
Performance Grade (PG)	ASTM D6373-16 [28]	1 × 25	1%
Multiple stress creep recovery (MSCR)	ASTM D7405-15 [29]	1 × 25	1%
Master curve	–	1 × 25	1%
Linear amplitude sweep (LAS)	AASHTO TP 101 [30]	2 × 8	1%

RTFOT to each temperature gauging of $G^*/\sin(\delta)$ parameter.

Master curves are used to express viscoelastic behaviour of asphalt binders according to temperature and load rate in wide frequency range based on time–temperature horizontal superposition principle; this methodology is already validated to SBS binders [31, 32]. Master curves test does not have a standard, therefore was used material response to applied loads as parameters to drive the tests. This search measured the frequency of torque application, dynamic shear modulus and phase angle to each master curve. Master curve uses a frequency range of 10^{-6} to 100 Hz.

Multiple stress creep recovery (MSCR) tests had 10 cycles of low tension (100 Pa) and 10 of high tension (3.2 kPa). Each cycle determines values of initial deformation ($\varepsilon 0$), peak deformation (εc), residual deformation (εr), deformation at 1second ($\varepsilon 1$) and deformation at 10 s ($\varepsilon 10$). With these data values of percentage of elastic recuperation ($\%R$), non-recovered compilation (Jnr) and susceptibility to deformation (Jnr) were calculated.

LAS test was performed according to standard American Association of State Highway and Transportation Officials (AASHTO) MP 19–10 (2012) [33] except for use of ageing by PAV due to technical limitations. Samples were refrigerated until 25 °C as recommended in the specific literature [34, 35].

2.3 Statistical Analysis

Statistical analysis was conducted through analysis of variance (ANOVA) in one way. ANOVA is capable to evaluate random effect and human influence over test, as well ANOVA can indicate if the variation of control factor affects test result. This analysis was conducted with significance level of 95%. Therefore, when the probability (p) that changing in the controllable factor levels promoting changes in test result is less than 5%, controllable factor is significant. In other words, for p low than 5% a variation in controllable factor implies in statistically variance in test result [36].

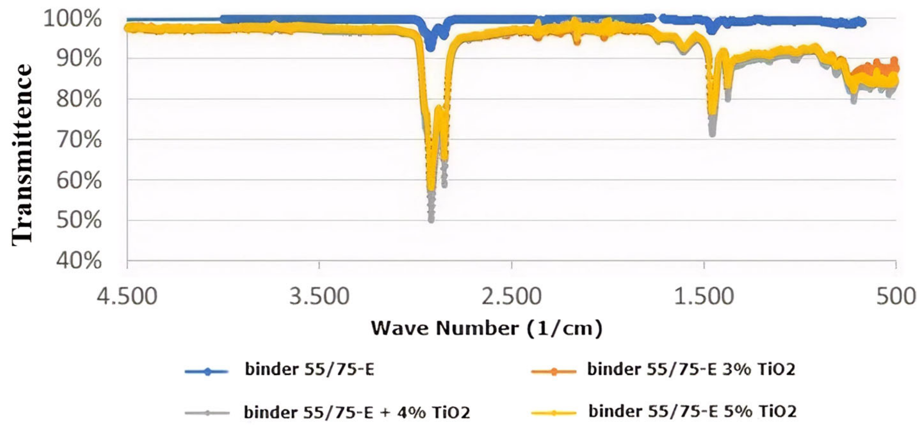

Fig. 4 FTIR of the 55/75 binder modified with TiO_2, overlapping curves to modified binders and short peaks to pure

3 Results and Discussion

3.1 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 4 shows the results of FTIR to pure binder and modifications with TiO_2. Peaks have high transmittance intensity to pure binder, while the modified binder has overlapping curves and peaks well-defined and with low transmittance intensity than pure binder. Pure and modified binder has peaks at same wave number range, 3.500 to 2.500. According to Marinho et al. [37], transmittance intensity difference can be due to test procedure interference. These two facts may suggest that TiO_2 addition did not performed any chemical alteration in pure binder. According to Elseifi et al. [38], peaks on range of 1600–400 cm^{-1} and 2920–2850 cm^{-1} may be related to asphaltenes. However, these bands, also, may be related to polar components of maltenes. Asphaltenes are related to asphalt binder rigidity, and maltenes are related to plasticity. Hence, FTIR is not conclusive if TiO_2 addition increase or lose plasticity in modified binders as well performed any chemical alteration.

Marinho et al. [37] Performed a FTIR analyses in a non-SBS binder modified with nano-TiO_2. The authors verified that nano-TiO_2 addition did not change characteristic peaks of chemical species wave number range, as well peaks transmittance intensity. Observing FTIR results of Marinho et al. [37], there is not a relationship between peak transmittance intensity and TiO_2 addition of non-SBS binder modified with nano-TiO_2. However, observing Fig. 4, TiO_2 addition in SBS binder lowered peak transmittance intensity. This fact suggests that TiO_2 addition behaviour in non-SBS and SBS binder is similar, as it did not change peak wave number range, but not equal, as it change peak transmittance intensity to SBS binder and did not to non-SBS binder.

3.2 Softening Point

Table 3 shows the result of softening point test to pure and modified binders. TiO_2 addition promoted an increase in softening point, on field this increase would result in improvements in resistance to permanent deformation. The same behaviour occurs when non-SBS binder is modified with nano-TiO_2 [37].

[13] modified an asphalt binder with 1%, 2%, 4%, 5% and 6% of nano-bentonite clay and nano-organically bentonite clay. Authors observed that softening point temperature raises as bentonite clay content raises. Softening point was 7% bigger than pure binder for organically bentonite and 5% to bentonite clay. Same behaviour, increase in sifting point temperature as increase nanomaterial content, was verified in this research as can be seen in Table 4.

3.3 Penetration Test

Table 3 shows the results of the penetration test to pure asphalt binder and modifications with TiO_2 before and after RTFOT process. According to Sun et al. [16, 39–41], reduction in penetration as nanomaterial is added is

Table 3 Softening point and penetration tests to pure and modified binders

Content of nano-TiO2	Softening point		Penetration	
	Before FTROT	After FTROT	Before FTROT	After FTROT
0%	52.0 °C	56.0 °C	0.562 mm	0.419 mm
3%	53.4 °C	57.0 °C	0.512 mm	0.370 mm
4%	54.0 °C	58.0 °C	0.476 mm	0.367 mm
5%	54.4 °C	58.0 °C	0.440 mm	0.340 mm

Table 4 Softening point and penetration test percentual variation relative to pure binder

Content of nano-TiO2	Softening point		Penetration	
	Before FTROT	After FTROT	Before FTROT	After FTROT
0%	0.0%	0.0%	0.0%	0.0%
3%	2.7%	1.8%	− 8.9%	− 11.7%
4%	3.8%	3.6%	− 15.3%	− 12.4%
5%	4.6%	3.6%	− 21.7%	− 18.9%

normal. This phenomenon may have occurred due to an addition of particulate loads to the asphalt matrix that promoted an increase on viscosity and rigidity of the material [37]. verified the same behaviour when modifying the non-SBS asphalt binder with nano-TiO_2.

Faramarzi et al. [42] modified an asphalt binder with carbon nanotubes with contents of 0.1%, 0.5%, and 1% of binder mass using dry and wet incorporation process. Authors verified that penetration depth reduced as carbon nanotubes rate increase. Binder with 1% of nanotubes showed penetration around 16% low than pure binder to dry mix process and 25% to wet process. Nofendra and Surmayanti [43] also modified asphalt binder, authors used 3%, 5% and 7% of nano-Al_2O_3. Authors verified that penetration reduced as content of Al_2O_3 increased. Binders with 5% showed the lowest penetration, 63% lower than pure binder. Penetration reduced with both nanomaterials suggesting that, with less or more efficiency, nanomaterials can reduce penetration values. Same behaviour was observed with nano-TiO_2 as shown in Table 4.

3.4 Rotational Viscosity

Figure 5 shows the result of viscosity, obtained through rotational viscosity test, to pure and modified binders.

Modified binders showed a bigger viscosity than pure binder before the RTFOT. However, after FTROT, modified binders got lower viscosities than the pure binder. This behaviour suggests that TiO_2 addition lowers binder ageing and avoids increase on viscosity values. According to Marinho et al. [37], a non-SBS asphalt binder modified with TiO_2 has a different behaviour. Authors verified that TiO_2-modified binder developed a viscosity greater than pure non-SBS binder, before RTFOT procedure. However, after RTFOT pure and modified non-SBS binders showed similar viscosity. Therefore, after RTFOT non-SBS and SBS binders modified with nano-TiO_2 had different behaviours.

3.5 Short-Term Ageing Procedure (RTFOT)

Table 5 shows results of retained penetration, softening point variation before and after RTFOT, thermal susceptibility index and mass loss after RTFOT. Modified binders had less loss of mass. This behaviour suggests less volatilization and preservation of viscoelastic proprieties.

According to Silva [44], retained penetration measures the capacity of a binder to keep its characteristics of penetration after RTFOT process. Modified binders got values of retained penetration higher than pure binder; all samples are around 70% of retained penetration. This fact suggests little alteration in material ageing susceptibility in short time. Table 5 also shows reduction of softening point variation; this fact suggests less ageing of modified binders.

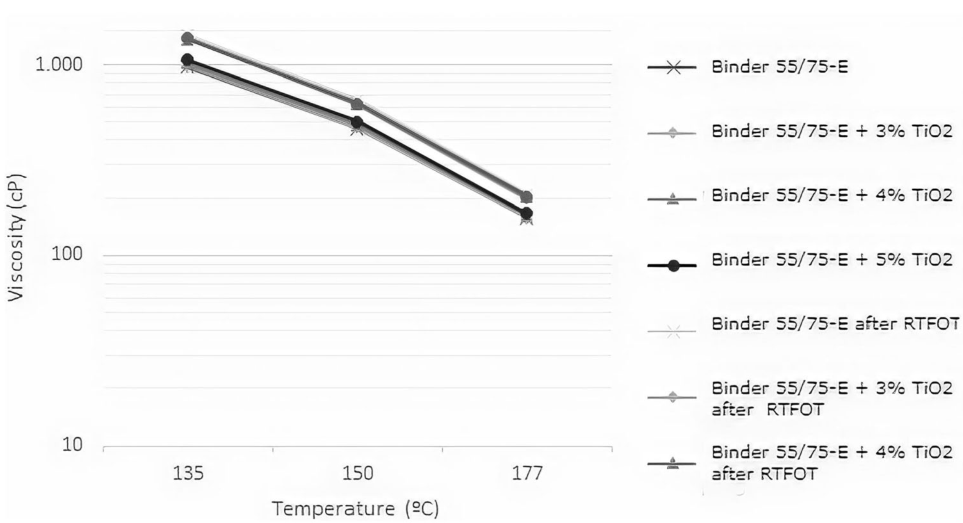

Fig. 5 Rotational viscosity test of binders, modified binders showed high viscosity than pure binders before RTFOT

Table 5 Properties of binders before and after RTFOT

Percentage of TiO_2	Retained penetration	Variation of the softening point before and after RTFOT	TSI	Loss of mass of binders submitted to ageing simulation RTFOT
0%	75%	3.5 °C	− 0.42	0.04%
3%	73%	2.5 °C	− 0.30	0.04%
4%	77%	3.0 °C	− 0.32	0.03%
5%	77%	3.0 °C	− 0.41	0.03%

Penetration and softening point tests allowed getting another parameter known as thermal susceptibility index (TSI). Most binders have a TSI between − 1.5 and 0 [45]. Table 5 shows that pure binder TSI was − 0.44, modified binders got values even smaller. Reduction of TSI suggests that modified binders tend to preserve its consistency over temperature variation more than pure binder.

RTFOT made all samples more rigid. This fact is reinforced for the reduction of penetration index and rise of softening point. Though, elevated rigidity is not desired because favours binder failure by fatigue.

3.6 Performance Grade (PG)

Figure 6 shows failure temperatures of continue PG to pure and modified binder. Failure temperature can be defined as the temperature at which parameter $G^{*}/\text{sen}\delta$ attain a value lower than 1 kPa. Modified binders obtained a reduction in the order of 3.6 °C in PG after RTFOT. Therefore, modified binders can be used at temperature lower than non-modified binder. This behaviour is not corresponding to non-SBS binder modified with nano-TiO_2 behaviour. According to Marinho et al. [37], nano-TiO_2 addition to non-SBS binder increases PG in 0.7 °C before RTFOT and did not not change PG after RTFOT.

Figure 7 shows ageing index (AI) of binders. AI is obtained by the relation between parameters $G^{*}/\sin\delta$ before and after RTFOT. Modified binders AI values are lower than the pure binder. This reduction indicates less volatilization of chemical components of asphalt matrix. Same behaviour was verified for Marinho et al. [37] with non-SBS binder modified with nano-TiO_2.

Facts above mentioned suggest that TiO_2 addition was beneficial to avoid oxidation of binder chemical components. This behaviour may be explained by high superficial area of the nanoparticles of TiO_2, which propitiate high interaction with particles of binder and carrying on reduction of oxidation tendency [46]. These facts reinforce results obtained in performance grade test. Reduction in oxidation reflects on great durability and economical gains of paving works. Similar behaviour was found for Marinho et al. [37] using non-SBS asphalt binder modified with TiO_2. Despite similarities, non-SBS binder modified with nano-TiO_2 got low reduction of AI than SBS binder modified with nano-TiO_2.

3.7 Multiple Stress Creep and Recovery (MSCR)

Figure 8 shows the results non-recoverable compliance (Jnr) for pure and TiO_2 modified asphalt binder, to tensions of 100 Pa until 3.2 kPa.

Figure 8 shows that Jnr decreases as TiO_2 percentage increases in both tension intensities. This behaviour indicates that modified binders are less susceptible to permanent deformations. According to Marinho et al. [37], non-SBS asphalt binder modified with nano-TiO_2 showed a different behaviour. Authors verified that with 100 Pa tension non-SBS binders modified with nano-TiO_2 showed

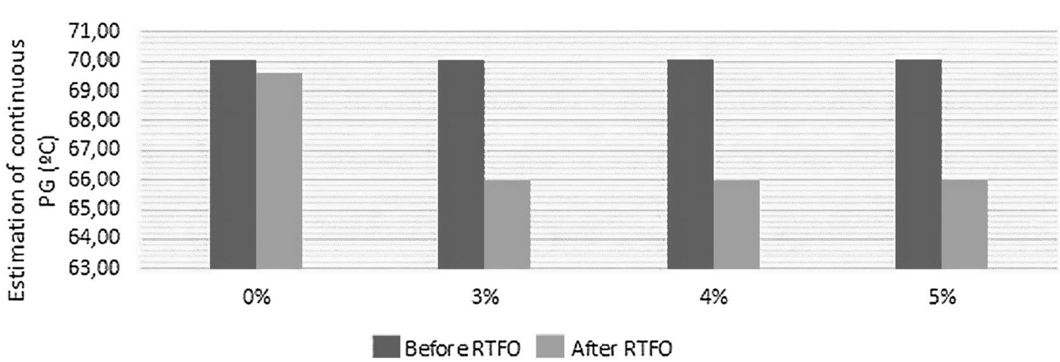

Fig. 6 Failure temperature estimation

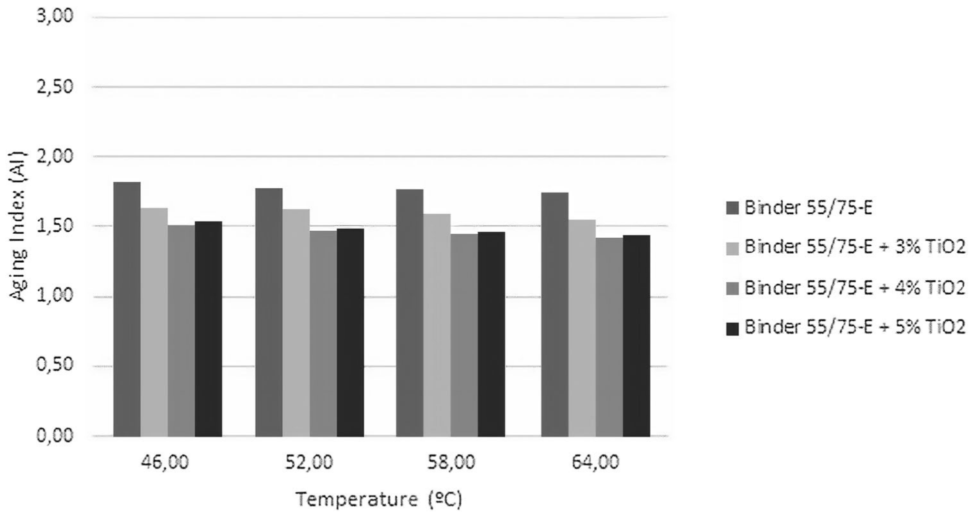

Fig. 7 Ageing index (AI)

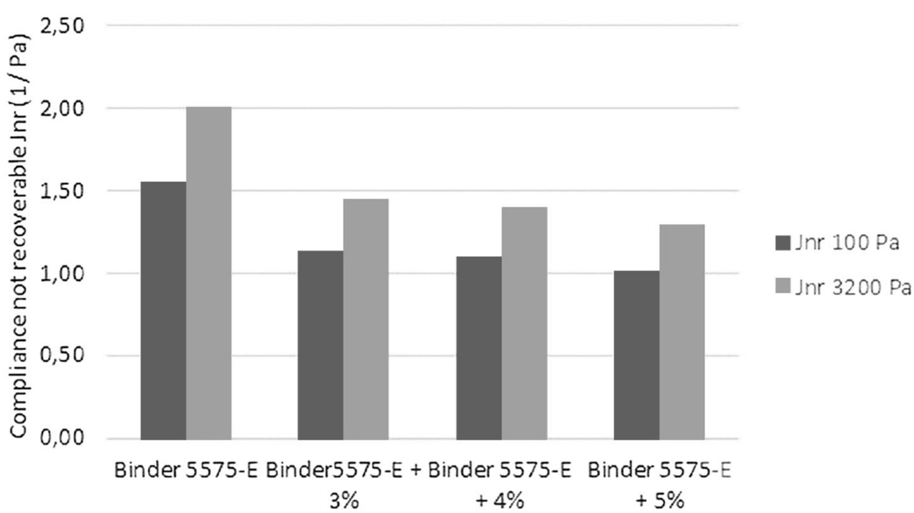

Fig. 8 Compliance not recoverable

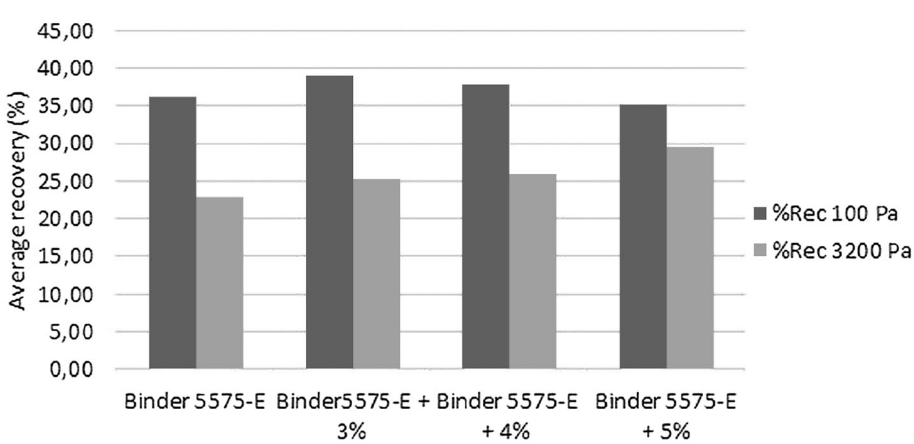

Fig. 9 Percentage of recovery at 100 Pa e 3.2 kPa

a significant reduction in Jnr, however at 3.2 kPa reduction was not significant.

Percentage of elastic recuperation (Rec) is shown in Fig. 9. Modified binders got recuperation bigger than pure binders. All the samples satisfied %Rec established by FHWA (2010) [47].

The increase in elastic parameter, with the addition of TiO_2, suggests titanium dioxide favours interaction between asphalt binder and SBS polymer. Asphalt binder with 5% TiO_2 showed a result like pure binder, this fact indicated bad dispersion of TiO_2. Jnr parameter measures susceptibility to permanent deformation. Therefore, Jnr reduction indicates low tendency of deformation.

The AASHTO MP 19–10 (2012) [33] specification says that difference between Jnr (Jnr diff) for 100 Pa and 3.2 kPa must be less than 75% to binders low sensible to abrupt tension variation. Modified binders showed lower values of Jnr diff than pure binders (Fig. 10). All samples were below 75%.

3.8 Linear Amplitude Sweep (LAS)

Table 6 shows an estimate for life of fatigue (Nf) for studied binders. Binder with 3% TiO_2 has got a better result than pure binder. However, the others modified binders showed Nf inferior to pure binder.

Figure 11 shows the relation between tension and deformation of binders. For deformation, among 0% to 22% pure binder got high projection peaks. This behaviour suggests superiority on support of deformations and applied tensions. Modified binders showed better behaviour than pure binders for deformations higher than 22%. Pure binder and modified binder got residual tension, characteristic that indicates good behaviour for application of tension and deformation.

Table 6 Estimated values for the life of fatigue

Amplitude of deformation (%)	1	2.5	5	10
Binder 55/75-E	262,500	25,772	4,453	769
Binder 55/75-E + 3% TiO_2	297,300	29,189	5,043	871
Binder 55/75-E + 4% TiO_2	201,300	19,909	3,459	601
Binder 55/75-E + 5% TiO_2	169,400	18,839	3,577	679

Nazari et al. [48] Modified an asphalt binder with 2% and 4% of nano-SiO_2, TiO_2 and $CaCO_3$. Authors observed that in stress–strain curve same behaviour observed in this research, nano-addition raise projection peaks and residual tensions.

Figure 12 shows damage characteristic curve to asphalt binder and modifications. Damage characteristic curve relates integrity parameter with damage intensity [49]. Therefore, damage characteristic curve indicates sample fatigue damage. All binders showed a similar behaviour. Despite similar behaviour, binder 55/75 + 3% TiO_2 got up the less satisfactory behaviour among all binders.

4 Statistical Analysis

ANOVA results are shown in Table 7

ANOVA to softening point before RTFOT indicates that TiO_2 addition did not implies in statistically variation in softening point before RTFOT. However, after TiO_2 addition statistically changes softening point value after RTFOT process.

ANOVA to penetration test before and after RTFOT indicates that TiO_2 addition implies in statistically variation in penetration. The p value before RTFOT is low than

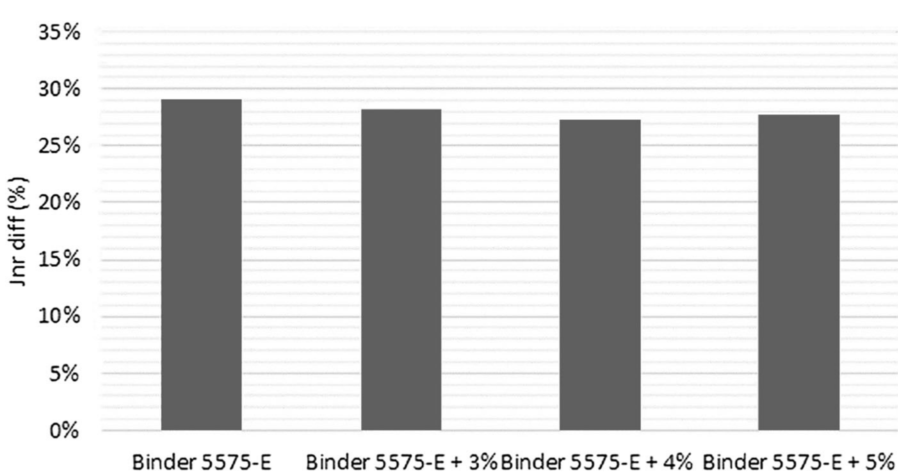

Fig. 10 Jnr diff

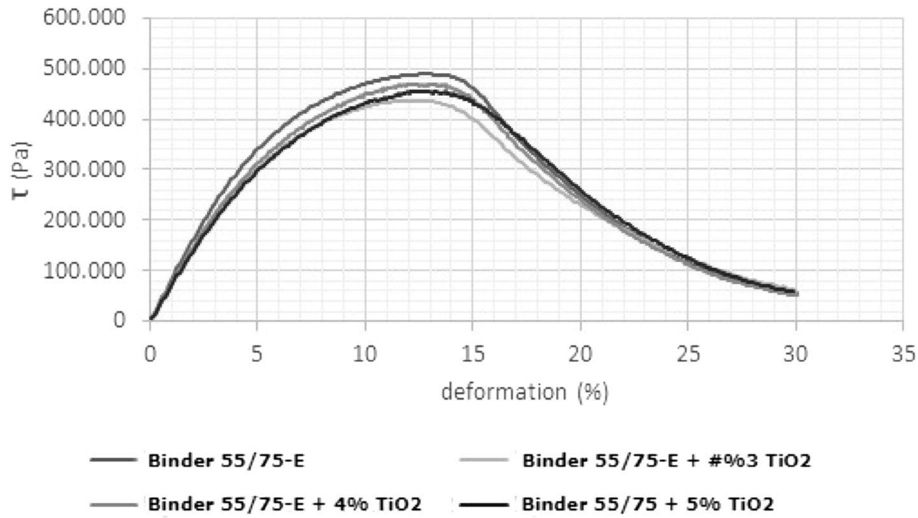

Fig. 11 Stress–strain curve

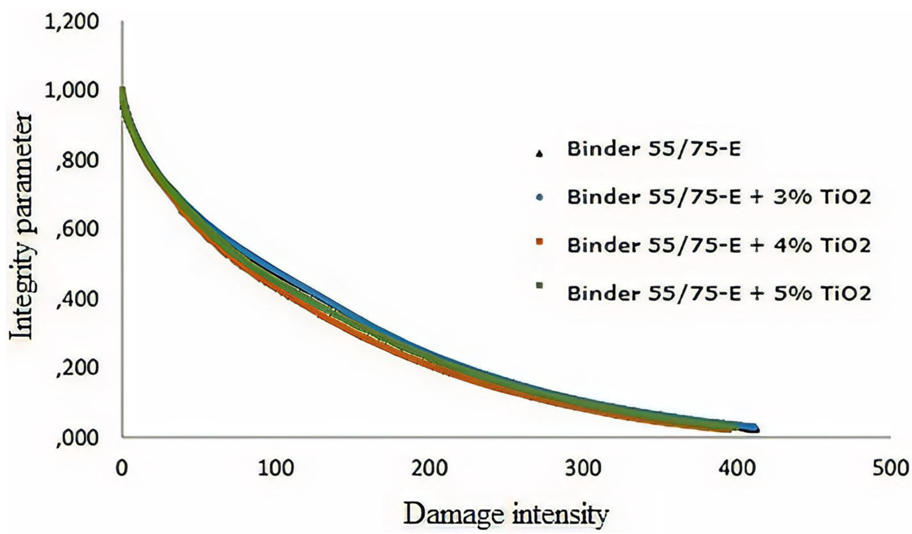

Fig. 12 Damage characteristic curve

after RTFOT; this fact means that TiO_2 incorporation is more significant in asphalt binders before RTFOT process.

ANOVA to viscosity indicates that TiO_2 addition is statically significant in both situations, before and after RTFOT and in all temperatures. However, after RTFOT TiO_2 incorporation influence in viscosity is greater than before RTFOT.

ANOVA to PG before RTFOT indicates that TiO_2 incorporation did not change PG. However, after RFOT TiO_2 promoted significant changes in PG after RTFOT. PG value is taken as the low value between PG before and after RTFOT in transportation engineering. Therefore, as PG after RTFOT was low than before RTFOT, TiO_2 addition can statically significant.

According ANOVA TiO_2 addition is statically significant to Jnr in both situations, 100 Pa and 3.2 kPa. TiO_2 addition is statically significant just with tension of 3.2 kPa to Rec. TiO_2 addition is not statically significant for Jnr diff. Therefore, TiO_2 incorporation did not affect recovery with low tension as well Jnr diff.

5 Conclusion

In this paper, authors analysed individually asphalt binder 55/77 penetration index modified with polymers and nano-TiO_2 by physical test and a chemical characterization by FTIR. After analysis, those materials are combined by mixing asphalt and TiO_2 in different contents to produce new asphalt binder samples. These new binders were chemical, rheological and physical analysed.

Table 7 ANOVA results

Test	Source of variation	SS	df	MS	F	p	F_{crit}	Sig. at 5% level
Softening point before RTFOT	% TiO_2	9.93	3	3.31	2.87	10.35%	4.07	NO
	Within	9.22	8	1.15				
	Total	19.15	11					
Softening point after RTFOT	% TiO_2	8.10	3	2.70	4.39	4.20%	4.07	YES
	Within	4.93	8	0.62	-	0.00%	-	
	Total	13.03	11					
Penetration test before RTFOT	% TiO_2	406.95	3	135.65	227.03	0.00%	3.24	YES
	Within	9.56	16	0.60				
	Total	416.51	19					
Penetration test after RTFOT	% TiO_2	161.65	3	53.88	49.95	0.00%	3.24	YES
	Within	17.26	16	1.08				
	Total	178.91	19					
Viscosity before RTFOT 135 °C	% TiO_2	27,564.06	3	9,188.02	6.36	1.64%	4.07	YES
	Within	11,562.50	8	1,445.31				
	Total	39,126.56	11					
Viscosity before RTFOT 150 °C	% TiO_2	5,564.25	3	1,854.75	6.64	1.46%	4.07	YES
	Within	2,234.67	8	279.33				
	Total	7,798.92	11					
Viscosity before RTFOT 177 °C	% TiO_2	348.50	3	116.17	5.03	3.01%	4.07	YES
	Within	184.67	8	23.08				
	Total	533.17	11					
Viscosity after RTFOT 135 °C	% TiO_2	34,642.56	3	11,547.52	18.67	0.06%	4.07	YES
	Within	4,948.67	8	618.58				
	Total	39,591.23	11					
Viscosity after RTFOT150 °C	% TiO_2	6,086.25	3	2,028.75	17.64	0.07%	4.07	YES
	Within	920.00	8	115.00				
	Total	7,006.25	11					
Viscosity after RTFOT 177 °C	% TiO_2	6,086.25	3	2,028.75	17.64	0.07%	4.07	YES
	Within	920.00	8	115.00				
	Total	7,006.25	11					
PG before RTFOT	% TiO_2	0.03	3	0.01	0.02	99.67%	4.07	NO
	Within	5.17	8	0.65				
	Total	5.21	11					
PG After RTFOT	% TiO_2	30.07	3	10.02	22.40	0.03%	4.07	YES
	Within	3.58	8	0.45				
	Total	33.65	11					
MSCR-Jnr 100 Pa	% TiO_2	0.51	3	0.17	74.42	0.00%	4.07	YES
	Within	0.02	8	0.00				
	Total	0.53	11					
MSCR-Jnr 3.2 kPa	% TiO_2	0.89	3	0.30	4.48	3.99%	4.07	YES
	Within	0.53	8	0.07				
	Total	1.42	11					
MSCR-REC100 Pa	% TiO_2	26.59	3	8.86	3.09	9.00%	4.07	NO
	Within	22.97	8	2.87				
	Total	49.56	11					
MSCR-REC 3.2 kPa	% TiO_2	65.11	3	21.70	8.03	0.85%	4.07	YES
	Within	21.63	8	2.70				
	Total	86.74	11					

Table 7 (continued)

Test	Source of variation	SS	df	MS	F	p	F_{crit}	Sig. at 5% level
MSCR-Jnr diff	% TiO_2	0.00	3	0.00	0.00	99.95%	4.07	NO
	Within	0.36	8	0.05				
	Total	0.36	11					

REC recovery

Tests showed that TiO_2 modified binders have developed more rigidity and increase softening point than pure binders. These facts suggest that modified binders can support works temperatures bigger than pure binder. TiO_2 also promoted the reduction of softening point variation and lowered viscosity values after RTFOT. These facts suggesting that TiO_2 retarded binder ageing.

TiO_2 modified binder demonstrated to be more tolerant to temperature variation than pure binder; this fact can be visualized in PG and TSI parameters. TiO_2 addition also decreased volatilization and oxidation of chemical components of asphalt matrix and increased resistance to permanent deformation.

SBS binder and non-SBS binder modified with nano-TiO_2 showed similar behaviour as in softening point and penetration tests, as well different behaviours as in rotational viscosity, PG and MSCR. This fact suggest that TiO_2 has interacted with SBS and consequently SBS binder modified with TiO_2 had a different outcome when compared to non-SBS binder modified with TiO_2.

ANOVA results shown that TiO_2 addition is significant in most cases evaluated. However, TiO_2 did not change asphalt binder behaviour response to softening point before RTFOT, REC at 100 kPa and Jnr-diff. These facts suggest that TiO_2 just improves asphalt binder after ageing and over high solicitations

Incorporation of nanoparticles of TiO_2 improves asphalt binder workability in higher temperatures as well ageing resistance. Therefore, TiO_2 modification can be an alternative to improve asphalt binder performance.

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Data Availability The Rheological Evaluation of Asphalt Binder 55/75-E Modified with Nanoparticles of Titanium Dioxide expression data set was downloaded from https://tinyurl.com/ybcejho2, and other data generated or analysed during this study are available from the corresponding author on reasonable request.

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