Rheological Analysis of Asphalt Binders Modified with Hydrated Lime and Titanium Dioxide Nanoparticles

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Abstract

The significant increase in traffic on paved roads has accelerated the deterioration of asphalt coatings. Because of this, the use of additives to modify the properties of the asphalt binder has been studied in order to improve the performance in relation to, mainly, permanent deformations and fatigue life. This work evaluates the changes in the rheological properties of CAP 50/70 modified with fractionated particles of hydrated lime and titanium dioxide nanoparticles, obtained from the use of a ball mill. For this purpose, the CAP 50/70 was modified with the addition of fractionated lime particles in the contents of 3%, 5% and 7% by weight of the pure binder and with 3% of ground nano TiO2 (180 nm). The modified samples showed less loss of mass in the short term aging, proving to be an antioxidant alternative. In addition, it was found that the modified binders provided an increase in G (stiffness parameter) and, consequently, in the maximum Performance Grade (PG) temperature, allowing the use of the studied binders at higher temperatures. The binder modified with a content of 5% hydrated lime presented better results in the tests of permanent deformation (MSCR and LAS). The decrease in TiO2 granulometry increased the integrity of the binder and made it more sensitive to deformations under temperature variations, however, milled titanium dioxide showed a positive result in increasing the resistance of the asphalt binder to fatigue when compared to the binder with nano TiO2 220 nm. Finally, it was possible to establish that the addition of fractionated particles of hydrated lime to CAP 50/70 is a viable and effective technique that meets the requirements of DNIT for use in paving and that the incorporation of ground nano TiO2 (180 nm) attributed to the asphalt binder 50/70 higher working temperature in the field.*

Keywords: Asphalt binder. Hydrated Lime. Nanoparticles. Titanium dioxide.

1. Introduction

The progressive increase in the volume of traffic, excess loads and the requirement of maintenance have contributed to the premature degradation of asphalt pavements. Due to the magnitude and repeated application of loads, over the time, pathologies develop in the structure of the pavements. These degradations occur mainly in the formation of permanent deformations and fatigue cracks.

An alternative to promote an increase in the useful life of pavements is the addition of modifiers of asphalt binders that increase the resistance to fatigue and minimize permanent deformations. For this, techniques have been used to modify asphalt binders, polymers, fillers, fibers and recently nanomaterials, which have shown technical and economic viability for this purpose. (MARINHO FILHO, 2017).

Nanotechnology involves the manufacture of structures, devices and systems with new properties and functions due to arrangements of their atoms on the scale of 1 to 100 nanometers or less. Among the nanostructured materials are nanoparticles, nanocrystals, nanowires, nanofibers, nanotubes and nanocomposites.

Previous research has used nanomaterials as modifiers of asphalt binders with positive results in improving the rheological properties and resistance to oxidative aging of the binders. Among these nanomaterials are inorganic nanoparticles such as silicon dioxide, titanium dioxide and calcium carbonate (NAZARI; NADERI; NEJAD, 2018), nanosilica and nanozinc (HONG et al., 2020), carbon nanotubes

(MAMUM; ARFUZZAMAN, 2018), copper oxide (AMINI; HAYATI, 2020), nanoclay (MORTEZAEI et al., 2020), and titanium dioxide (MARINHO FILHO, 2017).

Behbahani, Hamedi e Gilani (2020) used hydrated nano lime as an asphalt binder modifier and an anti-pickling agent to improve the resistance of asphalt mixtures. The results indicated that the use of lime showed an increase in the tensile strength and fatigue life of the mixtures, as well as an increase in the polar, non-polar and basic components of the asphalt binders and a decrease in the acidic components.

You et al. (2018) evaluated the dispersion of hydrated nano lime particles on foamed asphalt with water through physical-chemical analysis using scanning electron microscopy (SEM) and X-ray diffraction tests. It was concluded that the presence of lime hardened the asphalt and decreased the potential for bonding, as well as increased resistance to cracking at low temperature. Diab et al. (2013) used hydrated lime and nano lime (with sizes of 50 nm and 100 nm, respectively) to analyze the difference that would be obtained in the rheological properties of the asphalt binder for hot mixtures. The lime nanoparticles were added to the asphalt binder in proportions of 5%, 10% and 20% (by weight) and studied in the Dynamic Shear Rheometer (DSR). The authors concluded that the application of hydrated lime with a content of 20% by weight of binder can be replaced by the addition of almost 5% (by weight) of nanoparticles of lime (50 nm).

Nazari et al. (2018) studied the addition of titanium dioxide and silicon dioxide in asphalt binders and found a gain in resistance to aging. Theivasanthi (2017) states that the reduction in the size of the nanoparticles improves the mechanical, photocatalytic characteristics and TiO2 band gap that can be exploited in several applications. Zhang, et al. (2015) studied the rheological characteristics of the asphalt binder modified with expanded vermiculite and nano TiO2 and its results indicated improvement in the binder's resistance to aging.

Marinho Filho (2017) researched the effects of the incorporation of 3%, 4% and 5% of nano TiO2 in the pure state on the rheological characteristics of the 50/70 and 55/75 asphalt binders. In general, their results showed that the incorporation of nano TiO2 was beneficial to resistance to aging, decreased Jnr and increased resistance to fatigue, with emphasis on the content of 3% for presenting better results than the others. In order to reduce the agglomeration of particles in the binder, the superficial modification of the nano TiO2 was carried out with 3 different agents (oleic acid, benzyl alcohol and oleylamine). The rheological results performed on the incorporated binder with 3% of superficially modified nano TiO2 presented even better results in increasing the working temperature, lower aging rates and greater integrity of the binder when subjected to the induced damage, supporting greater numbers of cycles until failure by fatigue.

Based on the above, this study aims to compare the addition of hydrated lime with milled titanium dioxide in the asphalt binder by means of rheological tests.

2. Materials and Methods

This topic describes the materials and procedures performed during the experimental phase of the research, performed in accordance with AASHTO and ASTM standards.

2.1 Materials

CAP 50/70 Petroleum Asphalt Cement granted by the Rocha Cavalcante processing mill, located in the city of Campina Grande - PB, was used in the research. The Hydrated Lime used in the study was manufactured by the company Cal Norte Nordeste S.A. The nanoparticles with the trade name TiO2 - titanium dioxide FR 767 in rutile crystalline form were acquired through the company InterBrasil.

The lime needed to go through a milling process to acquire nanoparticle dimensions and, for this purpose, the methodology used by Kavussi and Barghabany (2015) was used, milling in the same equipment and with the same ball-to-dust ratio (BPR).

The centrifugal crusher mill used in the process was the periquito (parakeet), located at the Materials Engineering Laboratory of the Federal University of Campina Grande. In the procedure, milling was performed in a 5:1 proportion of BPR, in which 200 g of lime and 1 kg of balls (large and small) were placed in the mill for a period of 50 minutes, without using a milling control agent.

The TiO2 nano agglomerates easily due to its high surface energy. For this reason, for an efficient milling it was necessary to perform the wet milling with the use of hexane as surfactant for the nano TiO2. The study by Gajovic et al. (2002) on grinding TiO2 and ZrO2 in the choice of milling time and weight ratio TiO2-balls, was used as a reference . The 1:10 TiO2-balls weight ratio was used, totaling 100g of TiO2 nano and 30 ceramic balls of different diameters (1 kg). The milling time of 50 minutes performed in two stages of 25 minutes each, the interruption after 25 minutes was used to check the nano TiO2 agglomeration and it was observed that after the first 25 minutes the nano TiO2 was agglomerated. To continue the milling, a new TiO2 solution was made with hexane and milling was continued for another 25 minutes. At the end of the milling, the nano TiO2 was placed in an oven at 200 ° C to volatilize the excess hexane and dry the material. After the milling process, the particle size analysis was performed by laser diffraction of the nano TiO2.m.

2.1.1 Asphalt Binder

Table 1 shows the characteristics of the binders used before and after aging.

Table 1 - Properties of the asphaltic binder

Test	**Limits**	**Result**	**Standard**
Penetration 0.1 mm (100g, 5s, 25ºC)	50-70	54	ASTM D5:2019
Softening Point (ºC)	≥ 46	52	ASTM D36:2014
Rotational Viscosity (cP)	≥ 274 ≥ 112 57-285	430,00 (135°C) 219,50 (150°C) 83,00 (177°C)	ASTM D4402:2015
Residue Tests After RTFOT			ASTM D2872:2012
Mass Variation (%)	≤ 0,5	0,12	-
Softening Point Increase (ºC)	≤ 8,0	4,5	ASTM D36:2014
Retained Penetration (%)	≤ 55	74,34	ASTM D5:2019

The values obtained in the physical characterization tests of the asphalt binder before and after aging, were within the minimum and maximum limits required by the DNIT 095/2006 - EM standard in the penetration classification for the Petroleum Asphalt Cement CAP 50/70.

2.1.2 Lime

Table 2 presents the product specifications provided by the manufacturer.

Table 2 - Physical-chemical characteristics and lime granulometry used in the research

Physical-Chemical Characteristics	
Molecular weight	79,09
Percentage	> 90%
Melting point	510 °C
Relative density	2,24 g/cm³ a 20° C
Solubility in water	0,13 g/100ml de água a 17,8°C
Retention in # 325	≤ 1,5%
Granulometria	
D10	0,47 μm
D50	4,28 μm
D90	30,84 μm
Average diameter	9,87 μm

Source: Cal Norte Nordeste S.A

2.1.3 TiO2 nanoparticles

Table 3 presents the product specifications provided by the company. The TiO2 nano had an effective diameter in the range of 220 nm and a purity of about 90% (MARINHO FILHO, 2017).

Table 3 - Characterization of Nano TIO2 provided by InterBrasil

Item	**Specification**	**Result**
TiO_2	≥93	93.9
Whiteness (comparison with pattern)	Approximate	Passed on
Lighting Power (Reynolds Number)	≥ 1800	1940
R (%)	≥ 98	98,9
105 ºC Volatile	≤ 0,8	0,4
Water soluble matter (%)	≤ 0,5	-
pH	6,5 ~ 8,5	7,5
Oil absorption (g/100g)	≤ 21	20
Finesa % (45μ resíduo de peneira)	≤ 0,05	0,01

Dispersibility (%)		≥ 5,75	6,25
Resistivity (Ω.m)		≥ 80	261
Color	L	≥ 98	98,4
	B	≤ 2,4	2,06

Source: InterBrasil

This material is considerably used in the plastics and paints industries and must present certain characteristics for its use to be successful, such as lighting power, brightness, fineness and dispersibility. A avaliação realizada pela empresa determinou que o material enquadra-se nas especificações do padrão de qualidade internacional.

2.2 Methods

The experimental research program was performed in two stages: the first consists of the process of mixing the asphalt binder with the pre-established levels of the modifiers and the second stage corresponds to the analysis of the physical and rheological properties of the modified binders.

2.2.1 Mixing Procedure

The levels of lime used were based on the research by Saha and Nilufar (2010). According to the authors, the addition of particulate materials, with a percentage between 1 and 5% by weight, can improve the physical, mechanical and rheological properties of asphalt binders. Therefore, it was decided to incorporate the fractionated lime particles in the contents of 3, 5 and 7%, in addition to the reference binder, without incorporating the particles. The 7% content was determined as an additional study in order to analyze whether the addition has a positive effect on the rheological properties of the asphalt binder. The TiO2 content used was 3% based on the research carried out by Marinho Filho (2017) who concluded that among the levels of 3%, 4% and 5%, the content 3% obtained better results in the rheological tests performed.

The pure asphalt binder was placed in a mechanical mixer and heated to a temperature of 150 ± 5ºC. After the temperature stabilized, the modifiers were added to the binder, separately, and the mixtures were agitated by the propellers of the device at 2000 rpm for 90 minutes in order to ensure the homogeneity of the mixtures, slowly incorporating the percentage of each pre-established content in the binder.

2.2.2 Rheological Tests

The rheological properties of the modified asphalt binders were obtained using the DSR Discovery Hybrid Rheometer (DHR-1) at the Pavement Engineering Laboratory at the Federal University of Campina Grande. The FASTTRACK software, developed by TA Instruments, was used to perform the rheological tests

The PG (Performance Grade) test was performed on asphalt binders modified with fractionated lime and TiO2 nanoparticles (180 nm effective diameter) before and after aging in an RTFO greenhouse. For this purpose, binder samples were molded with geometry of 25 mm in diameter and 1 mm spacing between plates. It was performed with an initial temperature of 46 °C with a temperature increase of 6 °C, where the parameter G */senδ was verified at each temperature step. The values of G */senδ should not be less than 1.00 kPa for un aged binders and 2.20 kPa for asphalt binders aged in an RTFO greenhouse. The test is interrupted when the minimum values established for G */senδ are not reached. The software generates a report at the end of each test.

The MSCR (Multiple Stress Creep Recovery) was performed at two voltage levels 0.1 kPa and 3.2 kPa with 10 cycles at each voltage level. The temperature adopted for the performance of tests was that of PG because this is the limiting temperature for the good functioning of the binder according to the parameter G*/senδ analyzed. The charging and rest times, established as a rule, are 1 second and 9 seconds respectively for each cycle. It was performed with samples aged in the short term (RTFO) and uses the same geometry of 25 mm in diameter and 1 mm of distance between the plates, the same geometry used in the PG test.

The LAS (Linear Amplitude Sweep) test can be performed after the sample is aged in the short and long term. This work was performed only for samples aged in the short term. A geometry of 8 mm in diameter and 2 mm spacing between plates is used. Initially, the geometry was heated to 64 °C to ensure the sample adhered to the geometry. The test temperature used was 25 ° C based on the studies by Nascimento (2015) and Marinho Filho (2017). The procedure has two steps: frequency scanning from 0.2 to 30 Hz, with 0.1% deformation; and amplitude scanning, with the application of small torques at a frequency of 10 Hz. The loading is increased so that the deformation varies from 0 to 30%. Every 10 cycles each value of applied shear stress is recorded, as well as the values of phase angle and complex module (MARINHO FILHO, 2017).

3. Results

3.1 Milling

The granulometric analysis by laser diffraction was performed in order to check whether the hydrated lime particles reached diameters on a manometric scale, as well as the effective diameter of the TiO2 nano. Table 4 presents the granulometric analysis of lime by laser diffraction in liquid medium.

Table 4 - Granulometric analysis of cumulative percentages

	Hydrated lime	**Ground hydrated lime**
Diameter by 10%	0,47 µm	0,45 µm
Diameter by 50%	4,28 µm	2,29 µm
Diameter by 90%	30,84 µm	14,53 µm
Average diameter	9,87 µm	5,08 µm

According to Table 4, it can be inferred that after milling there was a decrease in the average diameter of 48.53% of the hydrated lime particles. However, a material is inserted on the manometric scale when its particles have a granulometry between 1 and 100 nm (nanometers) or less. Therefore, the ball mill milling process did not result in the production of nanoparticles.

Some factors may have contributed to this result. The non-use of the grinding control agent may have caused the particles to agglomerate, preventing fragmentation into smaller diameters. Another source of error to be considered is the milling time. Possibly, the time established for the procedure was not able to achieve the expected objectives. Despite this, the fractional particles obtained were used in the study as an additive to the asphalt binder for the analysis of rheological behavior.

Figure 1 presents the grain size distribution of nano TiO2, before and after milling, obtaining a positive result in reducing the particle size of the material, with a reduction in the effective diameter from 220 nm to 180 nm.

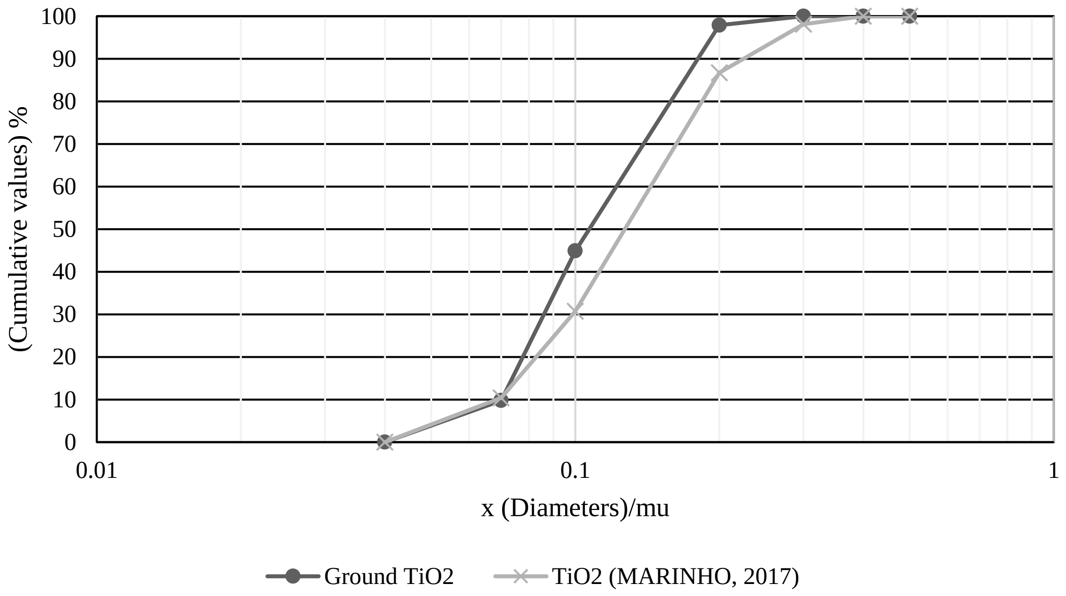

Figure 1 - Particle size analysis of TiO2 nanoparticles

3.2 Physical properties of pure and modified asphalt binders

3.2.1 Penetration Test

Figure 2 shows the results of the Penetration test for pure and modified binders with fractionated particles of hydrated lime and ground titanium dioxide nanoparticles, as well as before and after RTFO.

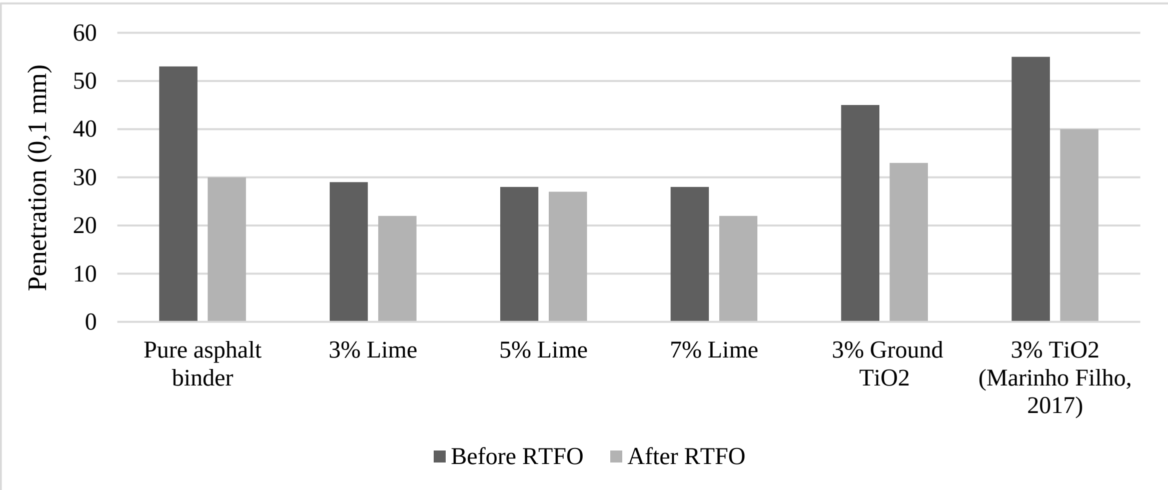

Figure 2 - Penetration Test for asphalt binders

It is noted that there was a significant decrease in the penetration values of the asphalt binders modified with the hydrated lime and with the ground titanium dioxide, in relation to the pure binder, showing an increase in the stiffness of the material with the addition of the modifiers. The penetration results for the titanium dioxide studied by Marinho Filho (2017) was quite similar to that of the pure binder.

Jahromi (2009), Ali et al. (2016), Sun et al. (2016) and Shafabakhsh and Ani (2015) raised that it is common to decrease penetration as fractionated particles are added to asphalt binders. According to resolution 19 of the National Petroleum Agency - ANP (2005), the classification range for the penetration values of CAP 50/70 binders is the interval between 50 and 70, where all the modified binders evaluated in this study did not reach the minimum value.

After the RTFO, there was a reduction in the penetration values, which is a recurrent feature of the binder aging. However, it can be noted that the addition in the content of 3% of TiO2 presented greater penetration among the modified binders analyzed, proving to be less rigid in relation to the other contents.

Figure 3 presents the values, in percentage, of the retained penetration (penetration ratio after and before aging). This data is important to verify the sensitivity of the binder to aging and for that purpose, ANP Resolution 19/2005 defines a minimum of 55% for this parameter. The closer to 100%, the smaller the change in the penetration value to aging, that is, the lower sensitivity to oxidation. Therefore, the modified binder with a 5% lime content showed the best result with a retained penetration of 96.4%.

All retained penetration values of the modified binders were higher than that of the pure binder. Therefore, the addition of fractionated particles from the modifiers contributed positively to the sensitivity of the binder, making it less susceptible to oxidation.

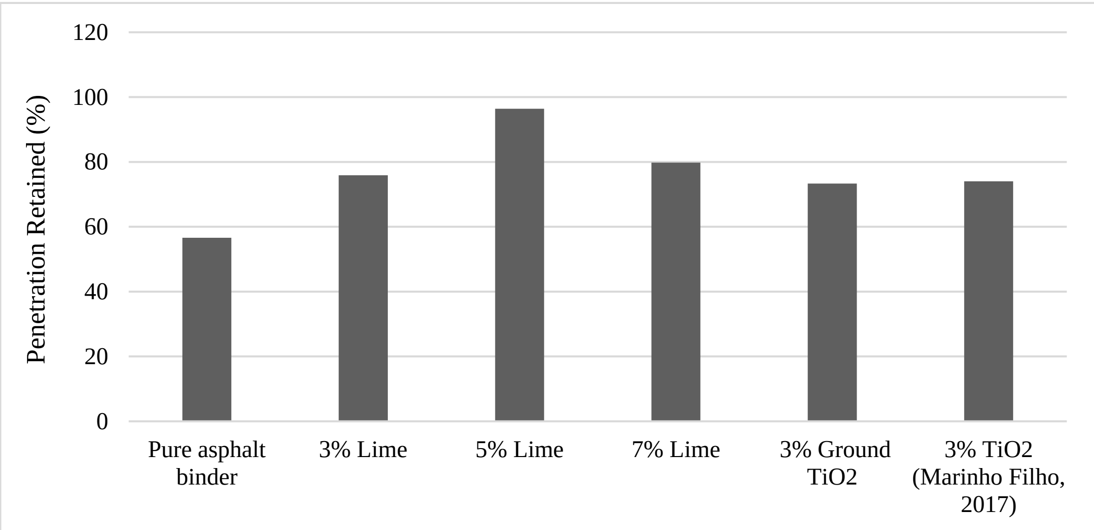

Figure 3 - Retained penetration ratio for CAP 50/70

3.2.2 Softening Point Test

The softening point is related to maintaining the properties of the binder at high temperatures and increasing the resistance to permanent deformation. This parameter was obtained from the average of the two test temperatures. Figure 4 presents the results of the softening point tests, when using pure binder and samples modified with fractionated particles of hydrated lime and titanium dioxide, as well as before and after RTFO.

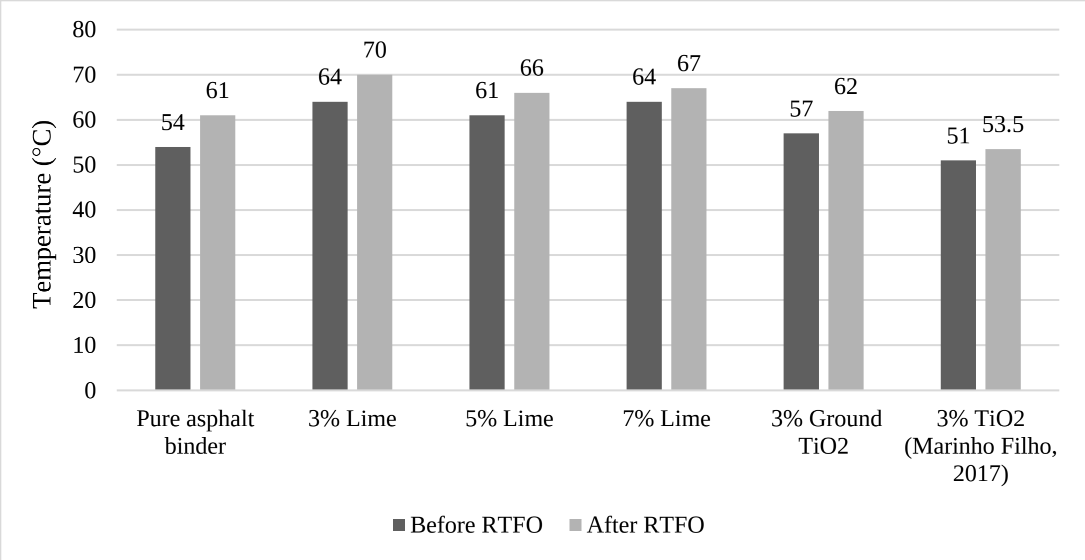

Figure 4 - Softening Point Values of CAP 50/70 samples

The ANP Resolution nº 19/2005 establishes a minimum temperature of 46 °C for the softening point in the normal condition, and thus, it appears that all binders have met this limit.

An increase is noted in the softening point in relation to the pure binder for all modified binders, in which the maximum temperature increase reaches approximately 10 °C, except for the one studied by Marinho Filho (2017). Among the levels used for the modification, the addition of 3% of TiO2 showed less value.

Figure 5 shows the variation of the softening points for the studied ligand (compared before and after the RTFO procedure). The DNIT 095/2006 Standard – EM determines that for CAP 50/70 the maximum softening point increase is 8 ºC. Among the results presented, it appears that the variations of all the modified ligands were lower than that of the pure ligand (7 ºC), probably caused by the addition of the modifiers.

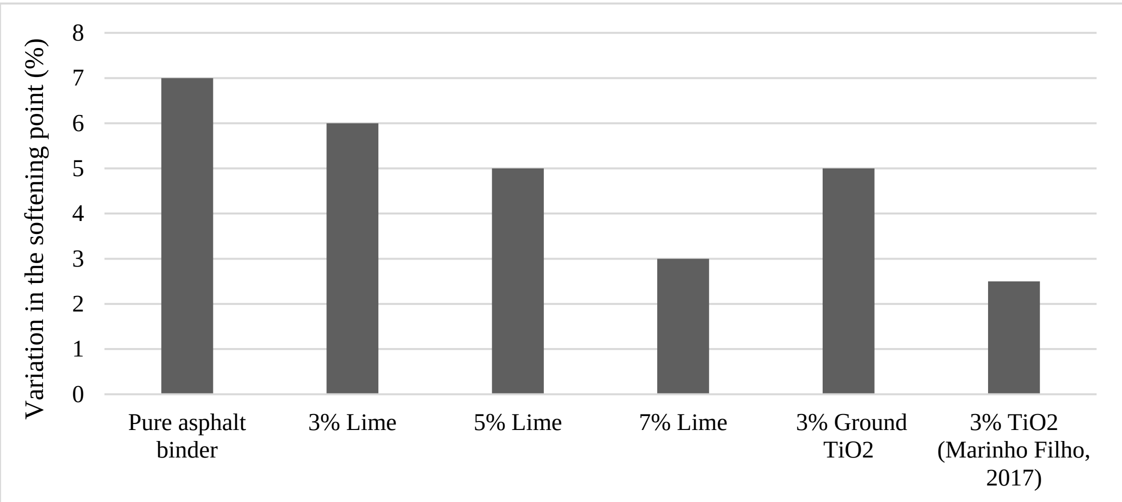

Figure 5 - Variation of softening points

The reduction in the softening point may be an indicative of less aging of the asphalt binder, since the softening point is related to the material's stiffness. The asphalt binders after the aging procedure are more rigid, and, therefore, have increases in softening point values.

The index of thermal susceptibility (ITS) is another parameter that can be analyzed from the results obtained from penetration and softening point. The ANP resolution (2005) establishes a range for the ITS values, ranging from -1.5 to +0.7 for binders without additions. Most asphalt binders have an IST between -1.5 and 0. Values greater than +1 represent oxidized binders, little sensitive to high temperatures and brittle at lower temperatures, while values less than -2 indicate binders that are very susceptible to temperature variations (BERNUCCI et al., 2006).

Table 5 shows the indices of thermal susceptibility for pure and modified binders. The data obtained are within the ranges established by the ANP and demonstrate that the binder modified with TiO2 studied by Marinho Filho (2017) has greater susceptibility than the other binders, however, the modified binders in this research have less susceptibility when compared to the pure binder.

Table 5 - Thermal susceptibility indexes of the ligand

	Pure asphalt binder	**3% Lime**	**5% Lime**	**7% Lime**	**3% Ground TiO2**	**3% TiO2 (MARINHO FILHO, 2017)**
Thermal Susceptibility Index	-0,36	0,59	-0,02	0,54	-0,45	-0,79

The binders with contents of 3% and 7% showed values close to the upper limit, characterizing them as binders with a greater possibility of becoming brittle. The addition of 5% fractionated particles of hydrated lime, for this analysis, presented a better result, as it kept the binder in a range closer to zero, which indicates that it became less susceptible to the effect of variation of temperature, an indispensable fact to guarantee the good performance of the pavement in the field.

3.2.3 Rotational Viscosity

Figure 6 shows the viscosity versus temperature graphs for the samples produced with the binder modified with particles of hydrated lime and titanium dioxide.

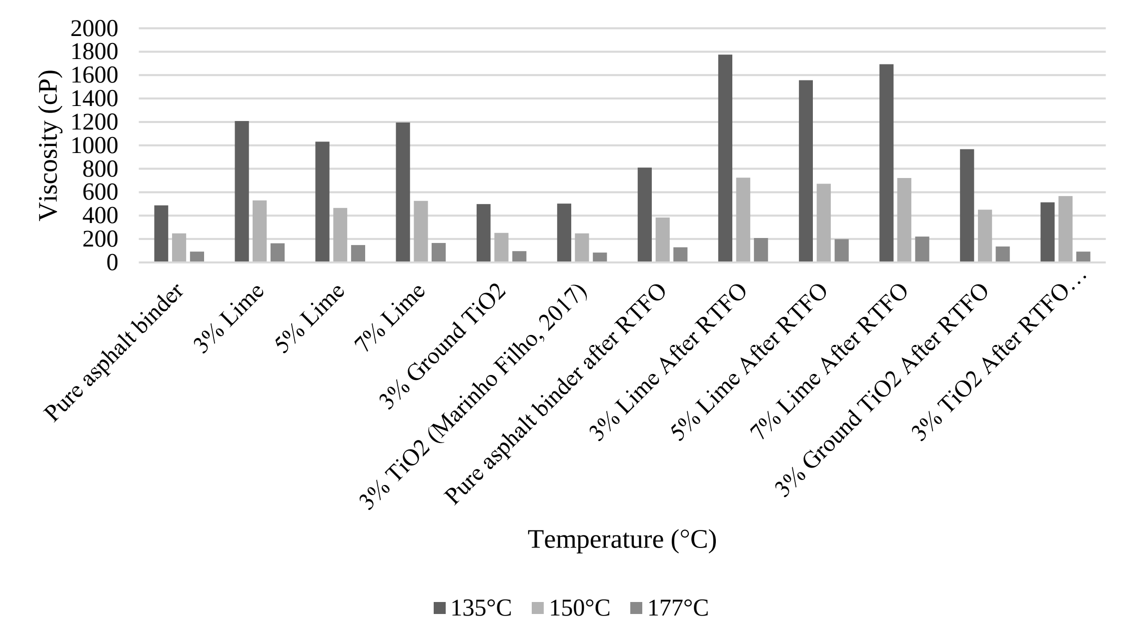

Figure 6 - Rotational Viscosity of modified CAP 50/70

The viscosity values of the pure binder, and consequently those modified by the addition of fractionated lime particles and titanium dioxide nanoparticles, assist the minimum values (274 cP - 135 °C and 112 cP - 150 °C) and range (57 to 285 cP - 177 °C) of the specification with their respective temperatures, according to ANP Resolution No. 19/2005.

In all levels there was an increase in viscosity, therefore all curves are above the pure ligand curve, except for the mixture analyzed by Marinho Filho (2007), which presented lower values. Analyzing the results, it is observed that the mixtures with 3% of TiO2 showed lower viscosity.

3.2.4 Short-term aging procedure (RTFO)

Figure 7 shows the results of the mass variations of the binders modified with fractionated particles of hydrated lime and titanium dioxide nanoparticles after performing the procedure in RTFO. The asphalt binders are in accordance with DNIT-095/2006-EM, which recommends mass variations of less than 0.5%.

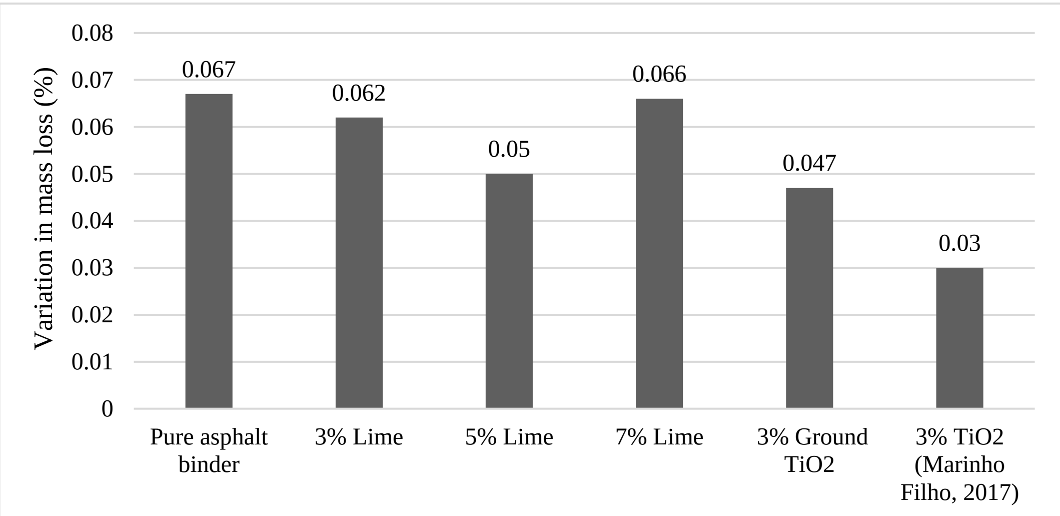

Figure 7 - Loss of mass of binders submitted to aging in RTFO greenhouse

When the binder is subjected to the aging process, it loses mass as there is a volatilization of the components that give it viscoelastic properties. In this way, the lower the mass loss, the greater the resistance to permanent deformations and the fatigue of the pavement. Analyzing the results, it appears that the mixtures that showed less loss of mass were those modified with a content of 3% titanium dioxide.

3.3 Performance Grade (PG)

The PG test was performed on an asphalt binder modified with TiO2 nanoparticles of 180 nm in effective diameter and with hydrated lime in the levels of 3%, 5% and 7%, before and after aging in an RTFO greenhouse. Figure 8 shows the PG temperatures (°C) for pure and modified binders.

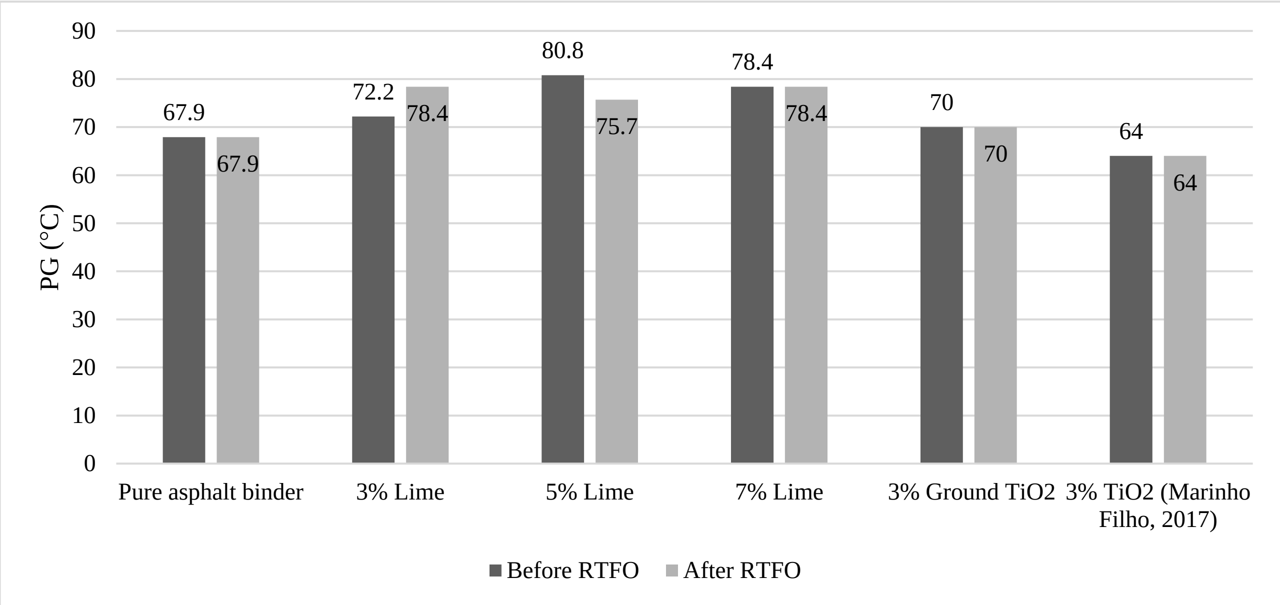

Figure 8 - Performance Grade for asphalt binders

It is noted that the addition of the modifiers analyzed in this research provided an increase in the maximum temperature of PG, highlighting the modified binders with lime that showed higher temperatures, especially the content of 5% of lime. This increase is interpreted by the increase in the Complex Module (G*), greater than the increase in senδ. The parameter G* corresponds to the stiffness and it is understood that there was an increase in viscosity in the modified samples allowing the achievement of a good Degree of Performance (PG).

The reduction in granulometry of the nano TiO2 was beneficial in increasing the binder failure temperature before and after aging in an RTFO oven compared to the pure binder and the nano modified TiO2 220 nm binder, studied by Marinho Filho (2017).

3.4 Test for multiple stress creep recovery (MSCR)

The test for multiple stress creep recovery (MSCR) allows to obtain the level of traffic supported by the binder and the percentage of binder recovery when subjected to tension variations. The higher the Jnr value, the material becomes more susceptible to permanent deformation. On the other hand, lower values of Jnr indicate resistance of the binder to this effect.

Figure 9 shows the Non-Recoverable Compliance values of the pure and binders modified with Cal and TiO2, with the application of a voltage of 0.1 kPa and 3.2 kPa.

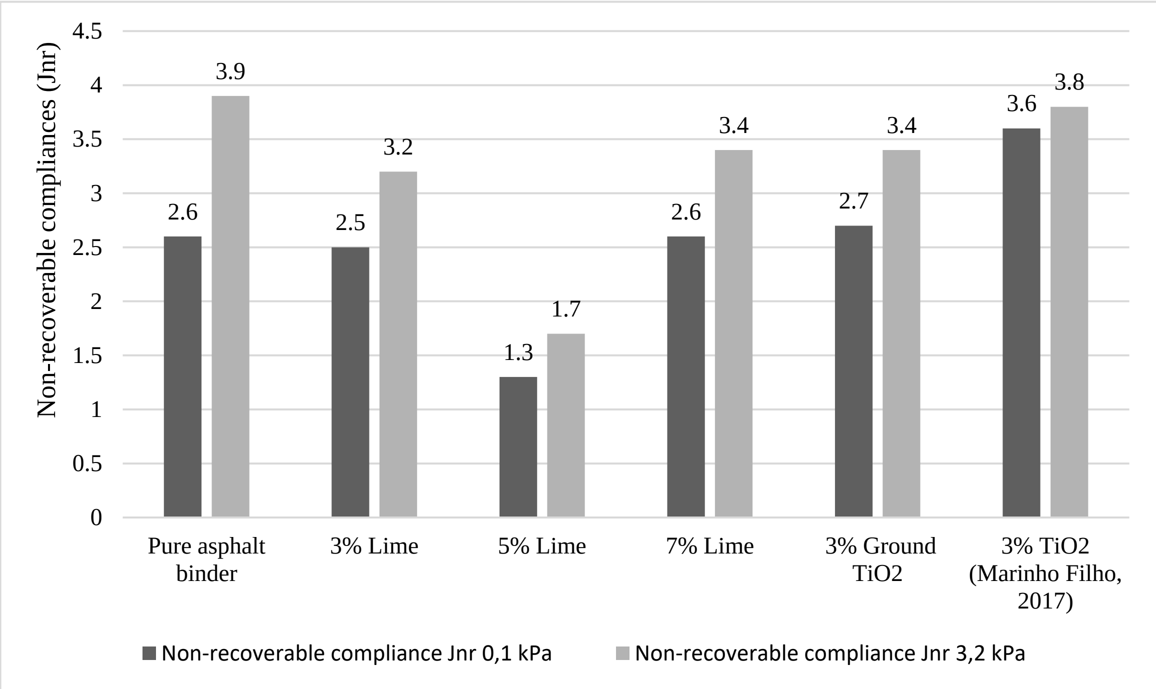

Figure 9 – Non-recoverable compliances from pure and modified binders

From the analysis of the Jnr values, shown in Figure 9, it can be noted that, with the application of the tension of 0.1 kPa and 3.2 kPa, the modified binder with lime in the content of 5% presents lower values for non-recoverable compliance when compared to the others, meaning to be the least susceptible to permanent deformation.

The non-recoverable compliance of the modified binder by 3% nano TiO2 180 nm is less than that of the pure binder at 3.2 kPa and that of the binder used by Marinho Filho (2017) modified by nano TiO2 220 nm at both 0.1 kPa such as 3.2 kPa. These results indicate that the decrease in the TiO2 granulometry for incorporation into the asphalt binder, compared to the binder used by Marinho Filho (2017), decreased the susceptibility to permanent deformations, as well as when compared to the pure binder.

According to AASHTO M320 (2016) it is possible to make the relationship between the values obtained for Jnr at 3.2kPa and the traffic class to which the binder is located. Table 6 presents this classification.

Table 6 - Pavement loading level classification based on Jnr values

Property	Jnr (1/kpa)	Type of traffic	Number of strides on a standard axis
Jnr at 3.2 kPa at maximum temperature of PG	2,0 – 4,0	Standard (S)	<10 Millions
	1,0 – 2,0	Heavy (H)	>10 Millions
	0,5 – 1,0	Very heavy (V)	>30 Millions
	0 – 0,5	Extremely Heavy (E)	>100 Millions

Source: AASHTO M320 (2016)

The pure binder is classified to support standard traffic (S), as well as the lime modified binders in the contents of 3% and 7% and the binders modified with 3% TiO2, as they have Jnr between 2.0 (1/kPa) and 4 (1/kPa). It is noteworthy that the binder with a 5% lime content was the only one to present a value between the limits of 1.0 (1/kPa) and 2.0 (1/kPa) and, therefore, classified to withstand heavy traffic (H), being the least susceptible to permanent deformation among the modified samples analyzed.

Another parameter analyzed in the MSCR test is elastic recovery. According to SHWA (2016) for binders with high Jnr, in other words, binders that have a high non-recoverable band, there is no specified minimum elastic recovery. The percentage of MSCR recovery (%) can identify and quantify the effect of the additive on the binder. An increase in the percentage values of this parameter results in the improvement of a modification of the binder to maintain elastic characteristics at high levels of traffic. Figure 10 shows the elastic recovery values for the binders modified with lime and titanium dioxide (TiO2).

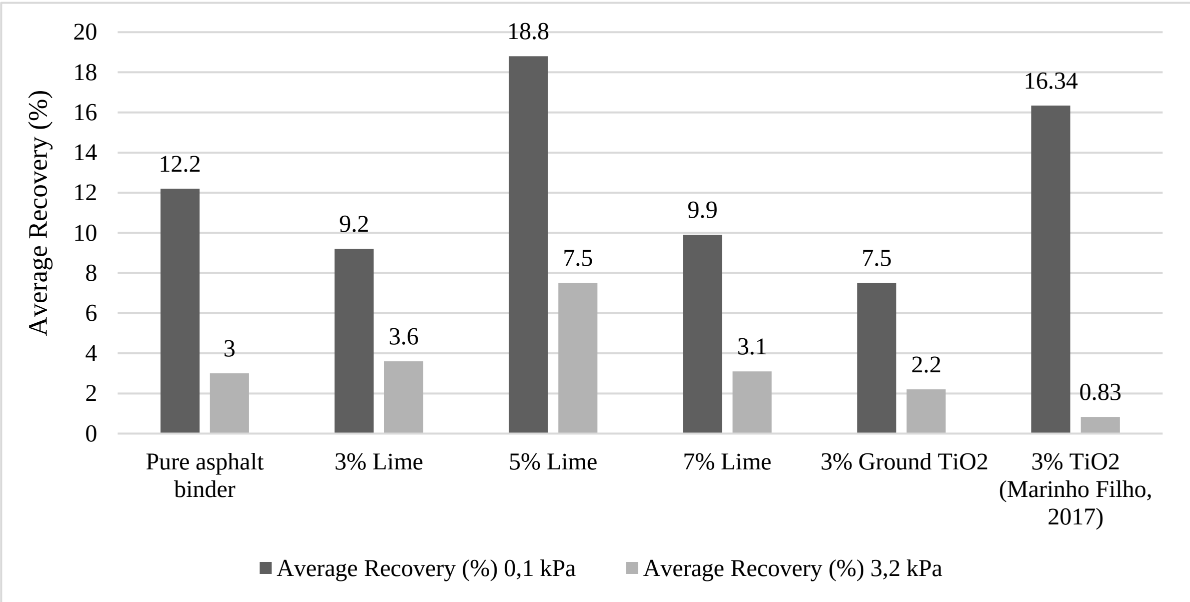

Figure 10 - Elastic recovery at 0.1 kPa and 3.2 kPa for pure and modified binders

The addition of lime promoted an increase in the recovery percentage of the material at the tension level of 3.2 kPa for all the samples, where the sample with 5% of lime showed the highest value. The increase in the elastic recovery of the mixture sample with 7% of modifier lime, at this level of tension, is insignificant because it presents a result similar to the pure binder.

In view of the analysis of the parameters of non-recoverable compliance and percentage of elastic recovery, the binder that presented the best results in relation to susceptibility to deformation and elastic recovery was the mixture with the addition of 5% of hydrated lime particles, presenting the ability to maintain its elastic characteristics at high traffic levels.

The milled titanium dioxide presented the lowest elastic recovery value when compared to the other studied binders, including the TiO2 nano analyzed by Marinho Filho (2017).

3.5 Linear Amplitude Sweep (LAS)

The linear amplitude sweep test is deterministic in ascertaining the fatigue life of asphalt binders. As a result, it presents two parameters: A and B. The A parameter, obtained by the amplitude sweep, is related to the variation of the material integrity due to the accumulated damage. Higher A values mean that the sample maintained its initial integrity. The B parameter, given by the frequency sweep, is related to the sensitivity to deformations. Figure 11 shows the variability of A and B parameters in the resistance to damage obtained through the linear amplitude sweep test for samples with CAP 50/70 modified with fractionated particles of hydrated lime and titanium dioxide.

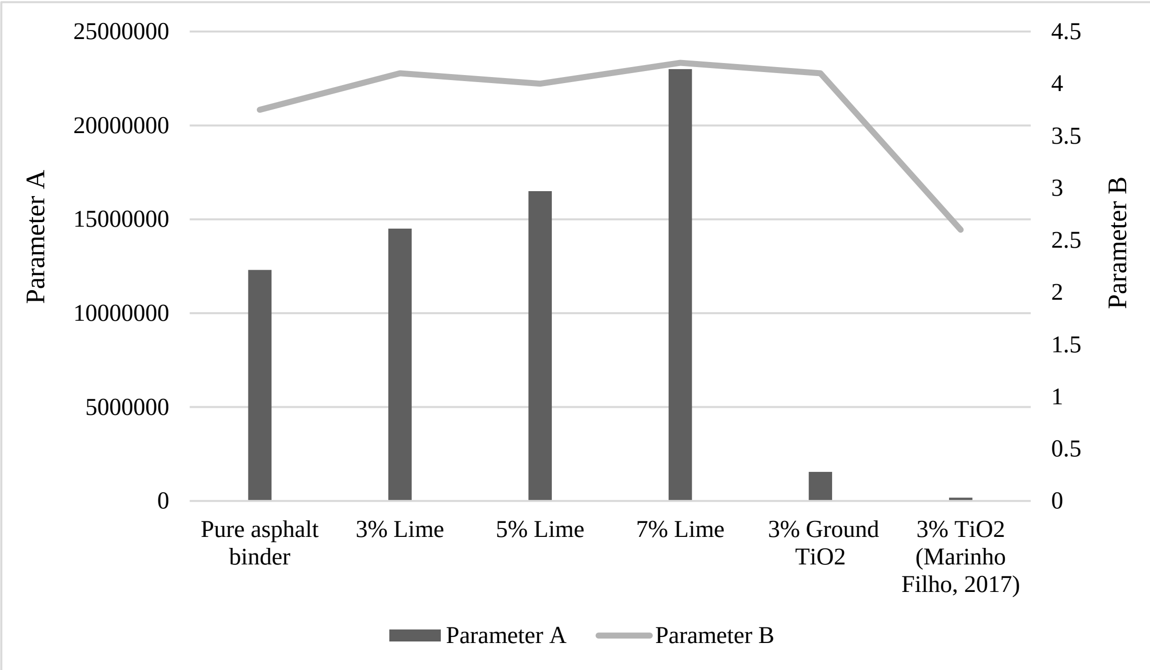

Figure 11 - Parameters A and B for pure binders modified with lime and TiO2

It can be observed in Figure 5 that there was an increase in the values of A parameter with the addition of fractionated lime particles in relation to the pure binder. In this way, the material that maintained the highest sample integrity was the modified binder with 7% of lime. In comparison to the pure binder, an increase of 87% in this parameter was obtained. The other levels obtained increases of 18% for the content of 3% of lime and 34% for the content of 5% of lime. The modified binders with titanium dioxide presented strong decreases in the A parameter when compared to the pure ligand and those modified with lime, the nano TiO2 220 nm being of lower value.

The B parameter, analyzed by means of the inclinations of the line shown, presents that among the modified binders, samples of modified binders with 3% TiO2 were more sensitive to deformation levels, which is not desired for asphalt binders. The sample with 5% hydrated lime showed the best result, with a lower inclination of the line. The analysis of the two parameters indicates that the decrease in the particle size of the nano TiO2 increased the integrity of the binder and made it more sensitive to deformations under temperature variations.

Figure 12 presents the fatigue life graph (Nf) as a function of the amplitude of deformation for asphalt binders in order to observe the effect of adding modifiers on the studied asphalt binder. Sobreiro (2014) apud Marinho Filho (2017) explains that the fatigue life indicates the volume of traffic that the material would support due to the deformation applied, while the deformation is related to the conditions in which the materials could be submitted in terms of the structure of the pavement.

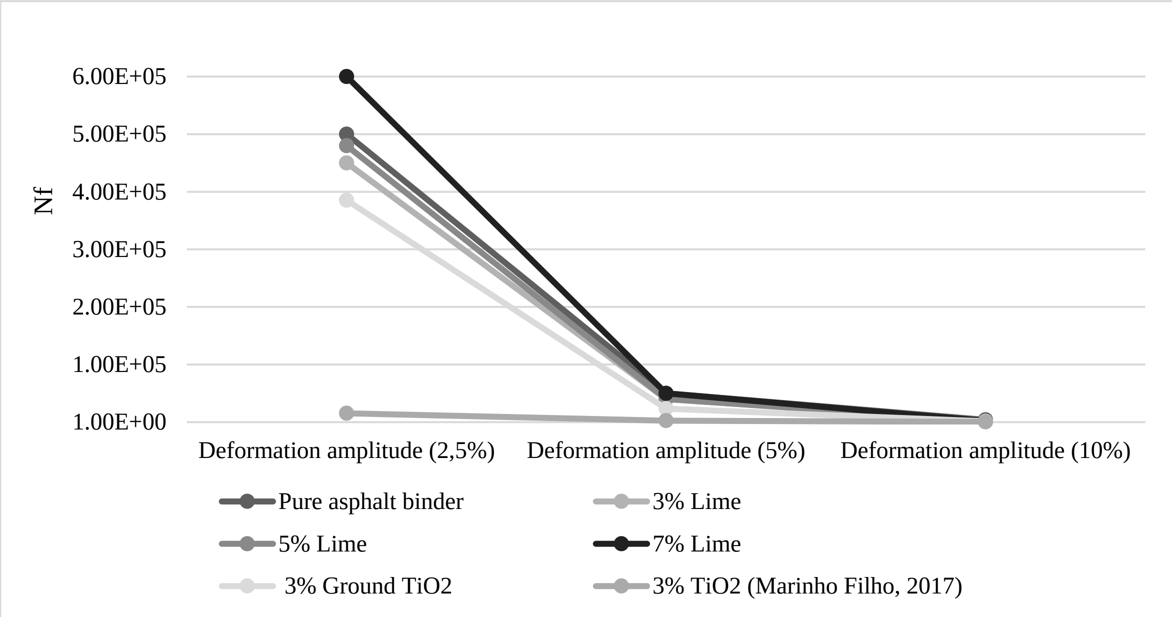

Figure 12 - Estimation of fatigue life of pure and modified binders

Based on Figure 12, it can be seen that the binder with 7% hydrated lime has the highest fatigue life estimates among all the analyzed binders. The Nf value of the sample modified with 3% milled titanium dioxide (180 nm) is greater than that of the modified ligand with 3% of TiO2 220 nm analyzed by Marinho Filho (2017), indicating that the decrease in the granulometry of the nano TiO2 proved to be positive in increasing the resistance of the asphalt binder to fatigue.

4. Conclusion

The milling process by the ball mill under the performed conditions (50 minutes long and without using surfactant) did not result in particles on a manometric scale for hydrated lime and the process with the use of hexane as a surfactant in the grinding of TiO2 is not advisable for not present significant improvements in the rheological characteristics of the asphalt binder.

The milling using a different surfactant and with a more expressive reduction in granulometry can still be used to study the influence of the size of TiO2 nanoparticles on the rheological properties of asphalt binders.

The modified binders showed better physical performance when compared to the pure binder. The mixture with 5% fractionated lime particles presented less susceptibility to oxidation and to the effect of temperature variation. The modified binder with 3% nano TiO2 presented lower viscosity and less loss of mass compared to other mixtures.

The rheological tests showed an increase in the performance level of modified binders with lime and nano TiO2 180 nm before and after aging in an RTFO greenhouse, obtaining higher failure temperatures.

The modified binder with a content of 7% hydrated lime showed better resistance to fatigue among the mixtures analyzed. Among the contents of hydrated lime studied and the use of milled titanium dioxide, the content of 5% of lime showed a lower value of Jnr, being classified to withstand heavy traffic and the other mixtures only for standard traffic.

The binders modified with hydrated lime showed higher values of the A parameter, indicating that the sample maintained its initial integrity. The decrease in the granulometry of nano TiO_2 increased the integrity of the binder and made it more sensitive to deformations under temperature variations when compared to nano TiO_2 220 nm. As for parameter B, the modified binder with a content of 5% hydrated lime presented less inclination and less susceptibility to permanent deformation, therefore, this mixture is the most suitable for use due to the good performance in all tests conducted.

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