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Investigation of titanium nanoparticles-reinforced Asphalt Composites Using Rheological Tests

Investigação reológica da de compósitos asfálticos pela incorporação de nanopartículas de dióxido de titânio

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ABSTRACT
Asphalt binder modification techniques are beneficial for the performance improvement of roads because they can be durable, present less permanent deformation, and provide longer fatigue life. The main modification agents involved in this process are polymers, fillers, fibers, and, more recently, nanomaterials, which have presented technical and economic feasibility. The nanoparticles were added to the base asphalt binder at a concentration of 3% of weight in pure and surface-modified states. This study aims to analyze the effect of surface modification of titanium dioxide nanoparticles using three different agents: oleic acid, benzyl alcohol, and oleylamine. The results have indicated that surface modification of the nanoparticles with oleylamine improved the interaction between the particles and the binder, contributing to increasing fatigue life and resistance to permanent deformation and delaying the aging process. Furthermore, the results of rheological tests have indicated that incorporating nanoparticles surface-modified with oleylamine into modified asphalt binder 55/75-E and asphalt binder 50/70 has produced higher resistance to the aging process less susceptibility to permanent deformation and cracks.

RESUMO
A modificação de ligantes asfálticos são benéficas para melhoria do seu desempenho em rodovias proporcionando durabilidade, menor ocorrência de deformação permanente e maior vida de fadiga. Os principais agentes utilizados neste processo são polímeros, fíleres, fibras e, mais recentemente, nanomateriais, que têm apresentado viabilidade técnica e econômica. As nanopartículas foram incorporadas ao ligante asfáltico na concentração de 3% em relação à massa de ligante nas condições pura e modificadas superficialmente. Este estudo tem o objetivo de analisar o efeito da modificação superificial das nanopartículas em ligantes asfálticos utilizando três diferentes agentes: ácido oleico, álcool benzílico e oleilamina. Os resultados indicaram que a incorporação das nanopartículas modificadas superficialmente com oleilamina nos ligantes asfálticos 55/75-E e 50/70 permitiram atingir maior resistência ao envelhecimento e menor suscetibilidade a deformação permanente e às trincas.

1. INTRODUCTION AND BACKGROUND

Modification of asphalt binders is commonly used to improve asphalt mixtures' rutting or cracking resistance. Consequently, it improves road safety and vehicle ride comfort and reduces maintenance costs. The National Cooperative Highway Research Program (NCHRP-459-2001) report entitled Characterization of Modified Asphalt Binders in Superpave Mix Design presents findings on using fillers, fibers, slag, and polymers as modifiers.

The application of nanotechnology in different fields has been growing exponentially in recent years. For example, Li et al. (2017) studied the application of nanotechnology to asphalt binders, addressing techniques to characterize the nanomaterials and tests to evaluate the modified binders. In addition, recent studies (You et al., 2011; Shafabakhsh et al., 2014; Golestani et al., 2015) reported the benefits of adding nanoscale materials to asphalt binders by allowing the application of nanotechnology in road constructions to solve long-standing problems in this field (Faruk et al., 2014).

A mixing method using water bubble escaping and bursting (water-foaming technique) and sodium dodecylbenzene sulfonate (C12H25C6H4SO3Na) as a surface modifier to improve the dispersion between Nano Hydrated Lime (NHL) and asphalt binder was developed by You et al. (2018). The authors revealed that the technique is a way to mitigate the agglomeration of nanoparticles and reduce mixing energy compared to traditional mechanical mixing methods.

According to Olsen (2013), titanium dioxide is one of the most common materials on the planet, about five times less abundant than iron and 100 times more abundant than copper. TiO2 is a metallic oxide, and it is common to use it in metallic oxides surface modifiers such as Oleic Acid (Alcantara, 2007; Viali, 2009) and Benzyl alcohol Oleylamine (Mourdikoudis & Marzán, 2013). The most common usage for this material is white pigment for paints; however, recent research studies have been testing titanium dioxide applications onto asphalt binders (Shafabaksh et al., 2014; Hassan et al., 2012).

Studies indicate that the addition of titanium dioxide nanoparticles to asphalt mixtures improves resistance against fatigue, permanent deformation, and oxidative aging (Shafabakhsh et al., 2014; Tanzadeh et al., 2013; Yang et al., 2018). However, Li et al. (2008) point out that the high surface energy of the nanoparticles leads to easy aggregation; this means that a treatment that produces better interaction between nanoparticles and asphalt matrices, improving dispersion would be efficient in increasing asphalt binder performance.

Zhang et al. (2015) tested three different nanoparticles (Titanium dioxide, silica, and zinc oxide) as asphalt binder modifiers. First, inorganic nanoparticles were surface-modified by silane coupling agents, which improve chemical adhesion between organic and inorganic materials. The results showed that surface modification of nanoparticles improved the compatibility and interaction of those particles with bitumen, leading to increased softening point and viscosity of the asphalt binder.

According to Hong et al. (2009), surface modification of nanoparticles can prevent aggregation, improve stability in suspensions and enhance the compatibility of nanoparticles with solid matrices. Therefore, Mahali and Sahoo (2019) performed tests to evaluate the effect of Nano TiO2 used as a modifier to modify Polymer Modified Binder (PMB) since both Nano TiO2 and SBS had individually shown positive effects on rheological properties when incorporated into asphalt binders.

Therefore, this work aims to study the effect of surface modification of titanium dioxide nanoparticles with different modifiers (oleic acid, benzyl alcohol, and oleylamine) on the rheological properties of asphalt binders.

2. MATERIALS AND METHODS

2.1. Asphalt binders

Asphalt binder 50/70 and Styrene-Butadiene-Styrene (SBS) modified asphalt binder 55/75-E were used in this study. These two binders were chosen because they are frequently used in the Northeastern region of Brazil. Table 1 presents the physical properties characterization of asphalt binder 50/70 and 55/75-E.

Table 1 – Asphalt binder characterization

Test		Method	Unit	Results	
				50/70	55/75-E
Penetration		ASTM D5	0.1mm	57	56
Softening Point		ASTM D36	°C	49	52
Rotational Viscosity	135°C, SP 21	ASTM D4402	cP	370	978
	150°C			184	464
	177°C			67.5	157
Elastic Recovery at 25°C		ASTM D6084	%	-	82
Mass Variation (RTFO)		-	%	0.04	0.05
Softening Point Increase		-	°C	3.5	3.5
Original Penetration Rate		-	%	75	77

Both asphalt binders meet the standard specification, except for the softening point criteria of binder 55/75-E, which was 3°C below specified. Mass variation tests and an increase in softening point and rate of original penetration were conducted after a Rolling Thin Film Oven Test (RTFO).

2.2. Nanoparticles

The nanoparticles used in this study were titanium dioxide (TiO_2 FR 767 classified as rutile). Its diameter varied from 10 to 150 nm. Table 2 presents the results of the tests performed on a titanium dioxide batch provided by its manufacturer (Interbrasil).

Table 2 – Nanoparticle characterization

Parameter		Results
pH		7.50
Oil absorption (g/100g)		20.00
Fineness % (45µ sieve waste)		0.01
Dispersibility (%)		6.25
Resistivity (Ω.m)		261.00
Chemical Composition (% mass)	TiO_2	90.37
	Al_2O_3	5.20
	Other oxides	4.43

The titanium dioxide nanoparticles' purity, particle size, and differential thermal analysis (DTA) levels were examined. The first two properties are related to the classification of the material as a nanoparticle. The DTA is related to the response of nanoparticles to temperature, allowing for evaluate the loss of mass due to thermal variation. DTA makes it possible to evaluate the thermal degradation of the material during the construction processes.

The sample of Nano TiO2 was subjected to X-ray fluorescence for chemical composition determination. The material went through a sieve with apertures of 0.18 mm, and the test was performed in Shimadzu EDX 720 equipment.

2.3. Surface modifiers

Nanoparticles can provide improvements over conventional materials. However, one of the problems encountered when working with these particle sizes is their agglomeration due to the high surface area/volume ratio, which makes the total free energy of the system high, resulting mainly from the high surface free energy of Gibbs. When particles have agglomerated, the effect of gravity on them starts. When their size reaches a critical value, the effect of gravity is dominant over the Brownian motion, resulting in precipitation (Beck Júnior, 2011). Therefore, to reduce this energy, particles tend to agglomerate or grow during synthesis (Medeiros, 2018; Sousa Neto, 2019).

The dispersion of a solvent determines the synthesis conditions and properties of the nanoparticles. A surfactant, which works as a stabilizer and passive agent of the surface of the particles, ensures their mono dispersion and prevents agglomerations (Magalhães, 2014).

These features quickly form agglomerates, where the particles group together and make it difficult to disperse in the desired medium. One way to minimize the low interaction between the nanoparticle and the dispersive medium is by modifying the surface of nanoparticles (Rong et al., 2006). Surface modification occurs through the physical graft adsorption coating, depending on the particle's surface properties. (Wang and Hong, 2011).

According to Li et al. (2008), it is important to promote the dispersion of titanium dioxide particles, as it has high surface energy, favoring particle agglomeration, taking the surface modification technique as a solution to this problem. The surface modifiers used during this work were oleylamine, oleic acid, and benzyl alcohol. Particles tend to agglomerate and decant due to the high surface energy of Nano TiO2. So, those surface modifiers were chosen to prevent nanoparticle agglomeration and avoid phase separation.

2.4. Test procedures

The first stage of the experimental program was the asphalt binder modification, which is based on the mixing procedure presented by Shafabakhsh et al. (2014), where the neat binder is placed into a mechanical mixer. Then it is heated to 150°C. Next, the nanoparticles are slowly added to the asphalt binder and mixed for 2 hours at 2000 rpm.

Before adding the asphalt binder modifier (Nano TiO2), those nanoparticles were surface-modified by using three different materials: oleic acid (C18H34O2), benzyl alcohol (C7H8O), and oleylamine (C18H37N). The main objective of the surface modification of titanium dioxide nanoparticles is to minimize the agglomeration of particles and facilitate their dispersion within an asphalt matrix.

The modification was made by employing magnetic stirring for 4 hours at room temperature with a proportion of 1:2 Nano TiO2 to the dispersing medium. After this procedure, the samples were dissolved in ethyl alcohol and centrifuged for 10 minutes at 3,000 rpm. Afterward, the samples were placed on a stove at 60°C to volatilize the alcohol, leaving only the surface-modified nanoparticles.

A total of six samples were prepared, whereas three of them used asphalt cement 50/70 – and each of these was associated with one of the three surface modifiers –and the other three were prepared the same way, except they used asphalt cement 55/75. The samples were prepared with 3% Nano TiO2, in conformity with the studies of Marinho Filho (2017), according to which this content level showed the best results for those rheological properties.

These modified asphalt binders were subjected to the rheological listed in Table 3 to verify any interaction between titanium dioxide nanoparticles and the asphalt matrix.

Table 3 – Rheological test standards

Test	Standard
Performance Grade (PG)	ASTM D6373
Multiple Stress Creep Recovery (MSCR)	ASTM D7405
Linear Amplitude Sweep (LAS)	AASHTO TP 101-14

Based on studies carried out by Hintz (2013), the LAS test was conducted at 25°C. For the MSCR test, the temperature value was the lowest PG before and after RTFOT, 64°C.

3. RESULTS AND DISCUSSION

3.1. Differential thermal analysis (DTA)

The results obtained (Figure 1) include the occurrence of endothermic peaks at 300°C referring to the crystallization of TiO_2 that occurs in a wide range up to approximately 550°C, and a peak at 900°C that can be attributed to the phase change of TiO2 anatase in rutile. The presented mass loss is related to dehydration and polymerization condensation process.

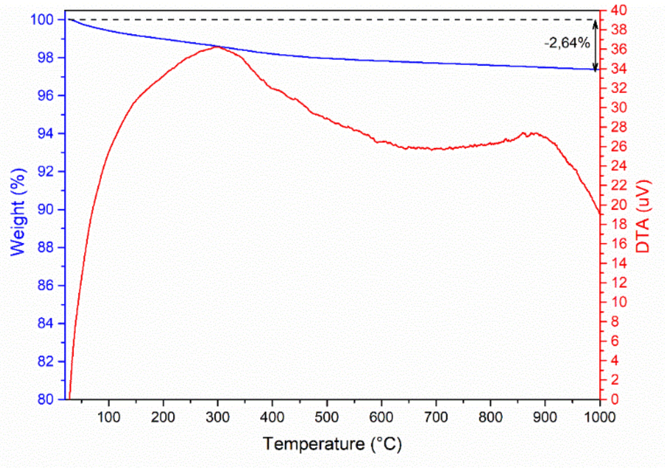

Figure 1. Differential Thermal Analysis (DTA) for TiO_2

3.2. X-Ray Difraction

X-Ray Diffraction (XRD) is used to determine the material's crystal structure. Figure 2 shows the crystalline structure of the TiO_2 and the presence of only TiO_2 peaks. In addition, x-ray efflorescence confirmed the purity of the material by indicating 90.37% of TiO_2.

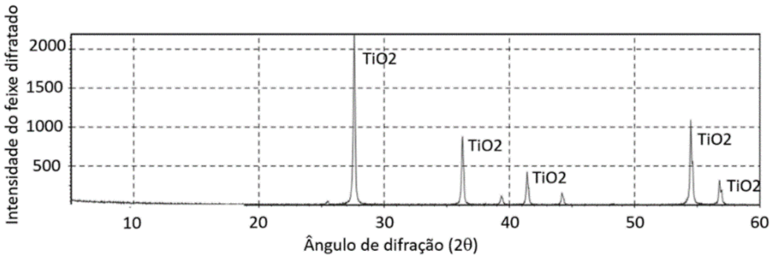

Figure 2. X-Ray Diffraction of TiO_2 Particles

3.3. Fourier transform infrared spectroscopy (FTIR)

The FTIR analysis was performed to verify if any chemical changes are induced by Nano TiO2 incorporation to asphalt binders 50/70 and 55/75-E, considering their conditions before and after the aging process. It is a technique that allows the evaluation of C-H, C-O, C=C, C-N, C-S and N-H bonds. Therefore, it is ideal for the evaluation of organic components or functions and their types of binding. However, it is not sensitive to metal-oxygen "bonds". For peaks and bands of inorganic components, as is the case of TiO2, they cannot be visualized in this technique.

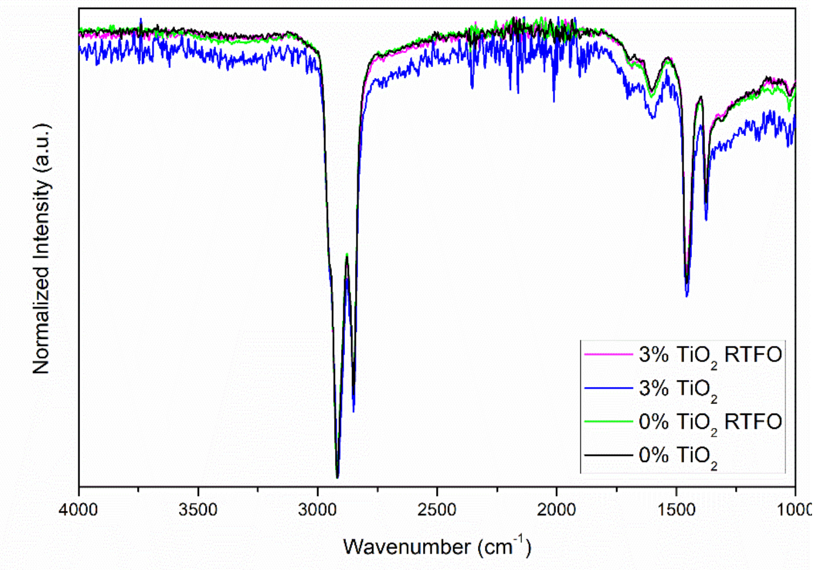

Figure 3. FTIR analysis for asphalt binder 50/70

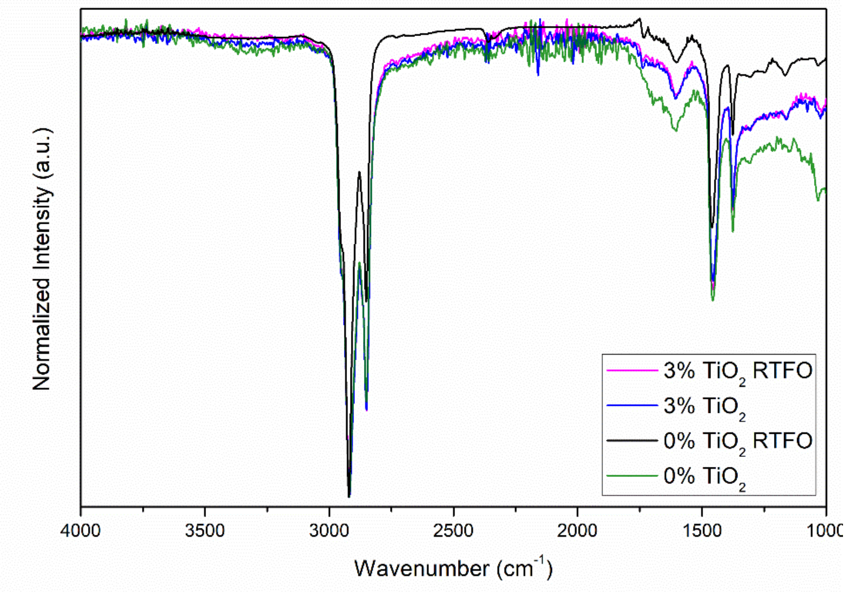

Figure 4. FTIR analysis for asphalt binder 55/75-E

Figure 3 shows FTIR spectra for the asphalt binder 50/70 based on transmittance peaks behavior for each sample. Both unmodified samples and 3% Nano TiO2 asphalt binder 50/70 presented significant transmittance peaks after the RTFO procedure. However, those peaks are larger for the pure sample when compared to the sample containing 3% nanoparticles content.

We can notice a weak intensity band between 3200-3600 cm-1, referring to O-H stretching, a peak around 1700 cm-1 for carbonyls, and a peek at 1030 cm-1 for C-O bonds, indicating weak oxidation of binder in the aging process.

FTIR spectra for the asphalt binder 55/75-E are illustrated in Figure 4. The overlapping of transmittance curves indicates minor changes, such as the appearance of peaks related to oxidized groups in the binder, appearing peaks between 3200-3600 cm-1, referring to O-H stretching, a peak around 1690 cm-1 for carbonyls, and a peek at 1030 cm-1 for C-O bonds, related to the aging process.

3.4. Performance grade

This topic presents the performance grade results for the asphalt binder 50/70 (control), the binders with 3% unmodified nanoparticles, and the binders with 3% nanoparticles modified with each one of the three agents.

Figure 5 shows the results for the asphalt binder 50/70. It was verified that the surface modification of the nanoparticles caused an increase in the PG of the unaged samples. However, after RTFO aging, the samples presented PG values close to those with 3% unmodified nanoparticles. The most significant difference was observed in the samples with oleylamine-modified nanoparticles.

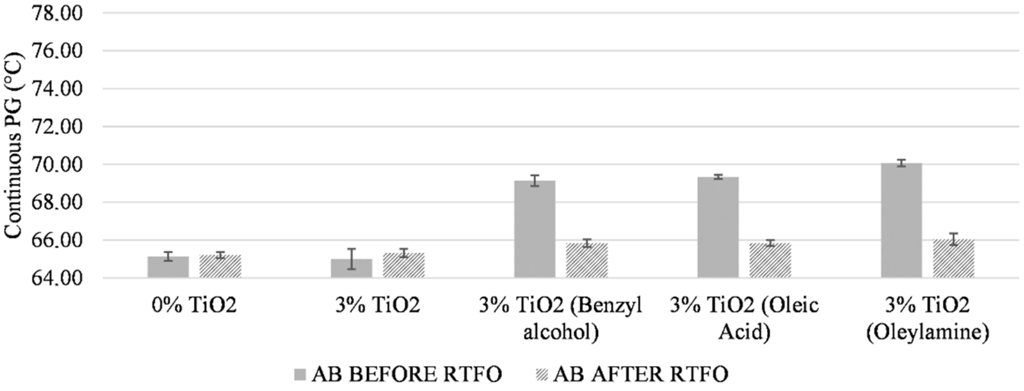

Figure 5. Performance Grade for asphalt binder 50/70 + 3% of modified Nano TiO_2.

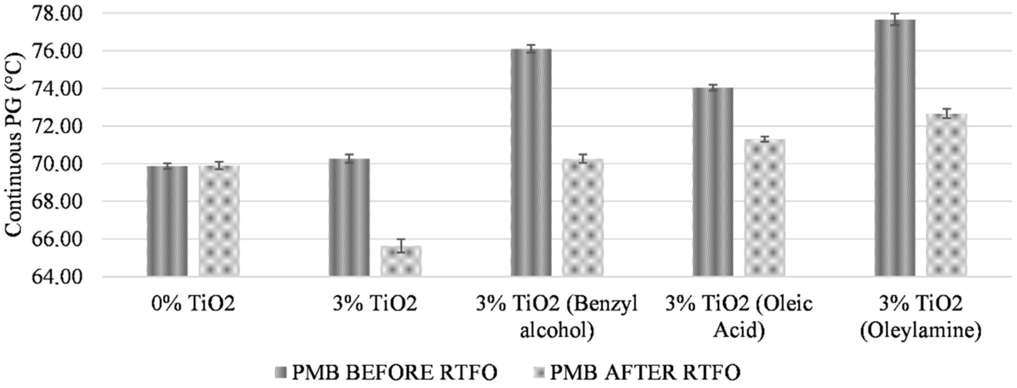

Figure 6. Performance Grade for asphalt binder 55/75-E + 3% of modified Nano TiO_2

Figure 6 presents the performance grades of samples with the 55/75-E binder. PG differences verified before RTFO were larger than those after the short-term aging. It was observed that after RTFO, the performance grade values have decreased, revealing an asphalt binder aging improvement with these chemical agents addition. The nanoparticles modified with oleic acid and oleylamine were the ones that promoted a greater increase in PG (1.9°C, and 2.6°C, respectively). This is a positive indicator that surface modification improved nanoparticle reactions within the asphalt binder, reducing agglomeration and improving dispersion in the asphalt binder matrix, as reported by Rong et al. (2006).

3.5. Aging index

The Aging Index (AI) was obtained from equation 1:

$$Aging\ Index = \frac{G^*/sin\delta(after\ RTFO)}{G^*/sin\delta(before\ RTFO)} \tag{1}$$

Figures 7 and 8 present the aging indices of binders. Figure 6 shows that the surface modification with all three agents benefited the nanoparticles' reaction in the asphalt matrix, retarding the aging of the binder. However, Oleylamine was the best performing agent, achieving a 53% lower aging rate than the neat binder.

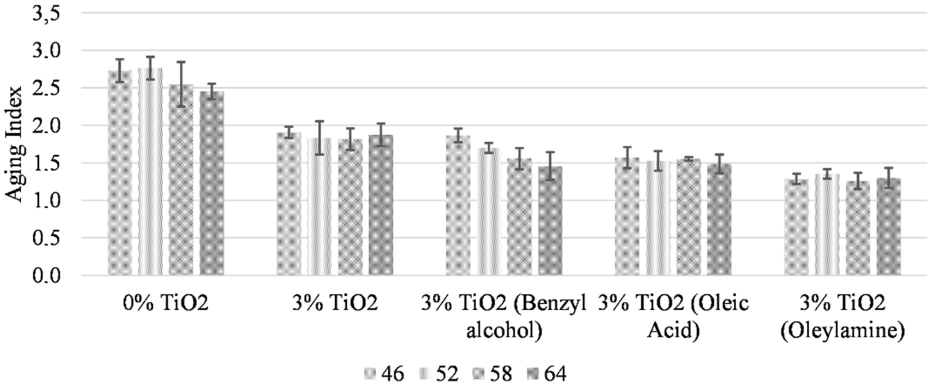

Figure 7. Aging Index for asphalt binder 50/70

Figure 8 shows that the action of the surface modifier agents on AI for the asphalt binder 55/75-E was not as significant as for the binder 50/70. The samples with benzyl alcohol-modified nanoparticles obtained aging indices 34% smaller than the pure binder. Samples with Oleylamine as a surface modifier showed a 22% reduction.

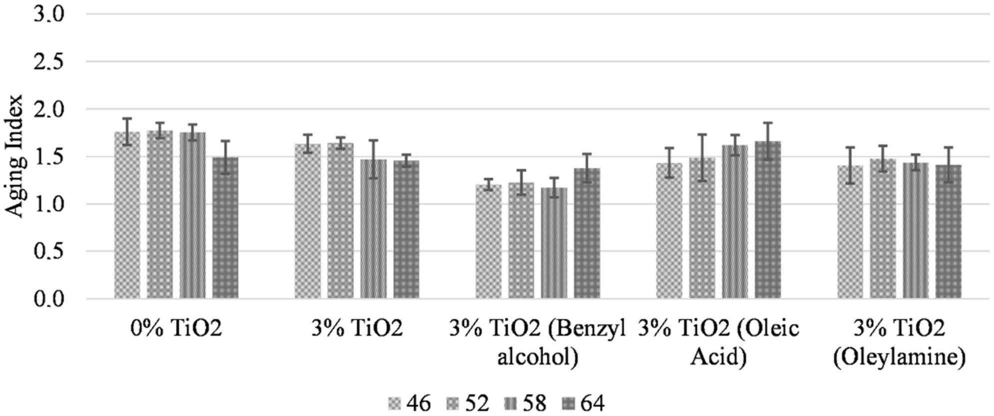

Figure 8. Aging Index for modified asphalt binder 55/75-E

Considering the aging index parameter analysis, the surface modification of titanium dioxide nanoparticles proved beneficial since it retarded the aging of modified samples. There was an increase in the PG of the binders, which means that they will meet failure criteria at higher temperatures than those tolerated by the non-modified binders.

3.6. Multiple Stress Creep Recovery

In this test, the parameters of non-recoverable compliance (Jnr) and elastic recovery were obtained, and surface modifications did not lead to significant variations in the elastic recovery of binders 50/70 and 55/75-E. These results were expected for the first binder since it does not have elastic properties based on the test criteria. Although, it was expected that the modification of the nanoparticles for the SBS binder would have caused better interaction between the asphalt matrix and the polymer, which would influence the elastic recovery parameter. Due to these conditions, this study deliberately leaves off values that would not add significant content to this work.

Figure 9 shows the values of the non-recoverable compliances for asphalt binder 50/70. It can be verified that the Jnr at high-stress level (3.200 Pa) decreased about 8% in the samples modified with benzyl alcohol and oleylamine. In contrast, its reduction was only 2.5% in the oleic acid-modified samples. This fact indicates that, despite small variations, benzyl alcohol and oleylamine have beneficial effects on the surface modification of the nanoparticles.

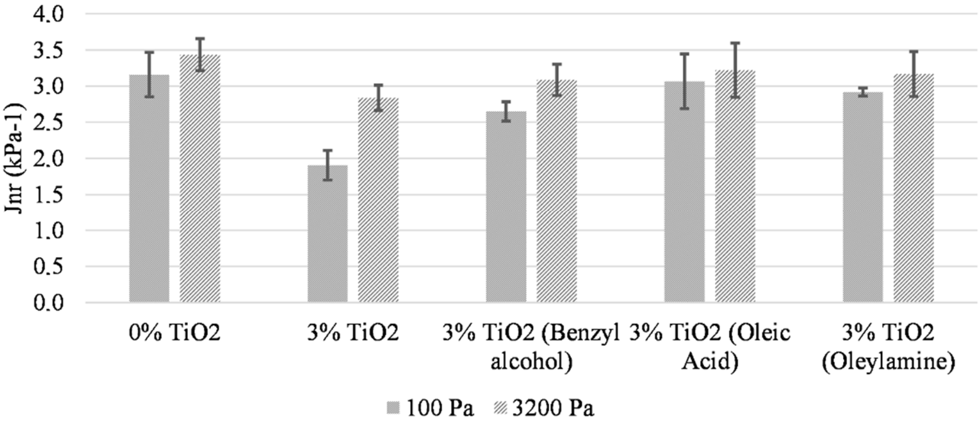

Figure 9. Non-recoverable compliance for binder 50/70 + 3% of modified Nano TiO_2

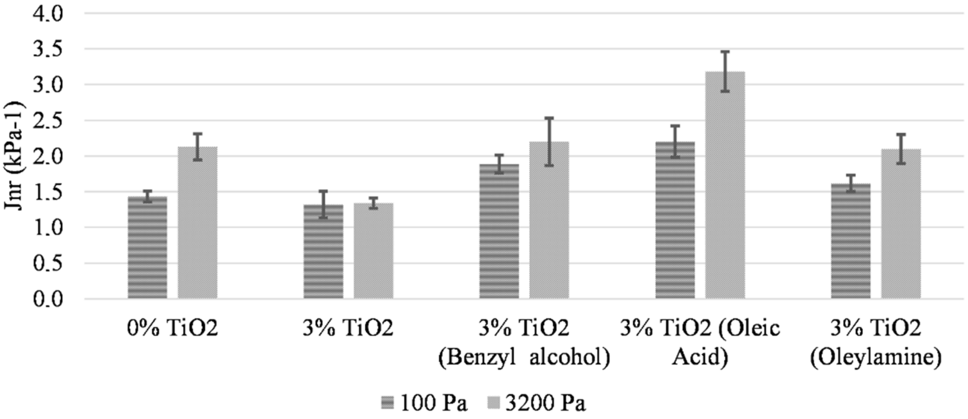

Figure 10. Non-recoverable compliance for binder 55/75-E + 3% of modified Nano TiO_2

Figure 10 presents the values of the non-recoverable compliances for asphalt binder 55/75-E. It was found that only oleylamine had positive effects on surface modification. The Jnr reduction was 5%, whereas the value of this parameter was increased for the samples modified with the other agents. In general, surface modification of the nanoparticles did not indicate improvement in the resistance to permanent deformation of the binders studied. Apart from the effect of surface modifiers, the modifier of asphalt binder 55/75-E (SBS) also promotes rheological properties by reducing Jnr values, leading to higher resistance to permanent deformation.

3.7. Linear amplitude sweep

LAS was performed according to AASHTO TP 101-14. In this test, parameter A represents material integrity as a function of cumulative damage, a model developed by Johnson (2010), in which the initial sample modulus (G*·sin) is reduced by about 35%. Therefore, the higher Parameter A is, the higher is fatigue resistance. Parameter B measures the strain sensitivity of the material. It is obtained from the frequency of sweepings and depends on the α value. Parameters A and B can be calculated through the following equations:

$$A = \frac{f(D_f)^k}{k(\pi C_1 C_2)^\alpha} \tag{2}$$

$$B = 2\alpha \tag{3}$$

Figures 11 and 12 present parameters A and B values for binders 50/70 and 55/75-E. It can be verified that oleylamine modification of Nano TiO_2 improved interaction of the latter with asphalt binder 50/70. Increases in the value of parameter A by 446% over the pure binder was observed, indicating an increase in damage resistance. Parameter B remained practically constant.

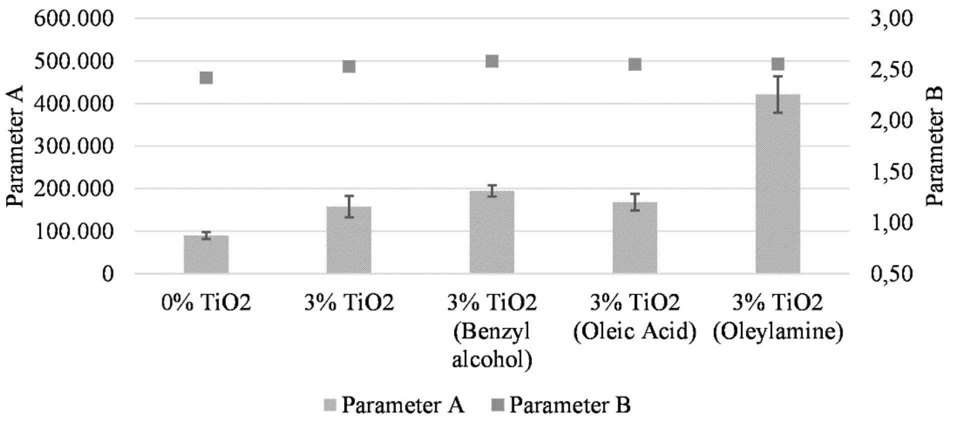

Figure 11. A and B parameters for asphalt binder 50/70 + Nano TiO_2

The addition of oleylamine-modified nanoparticles to binder 55/75-E showed the same positive results verified for binder 50/70 samples. The modification with oleylamine was the only one that provided damage resistance gains to the asphalt binder. Sensitivity to strain levels applied has shown a nearly constant performance.

Figures 13 and 14 show the graphs of fatigue parameter (Nf) versus shear strain for binders 50/70 and 55/75-E, respectively. The number of cycles to fatigue failure indicates the traffic volume that the material would support as a function of the load applied. In contrast, the strains were linked to the conditions these materials could be subjected to in pavement structure (Sobreiro, 2014).

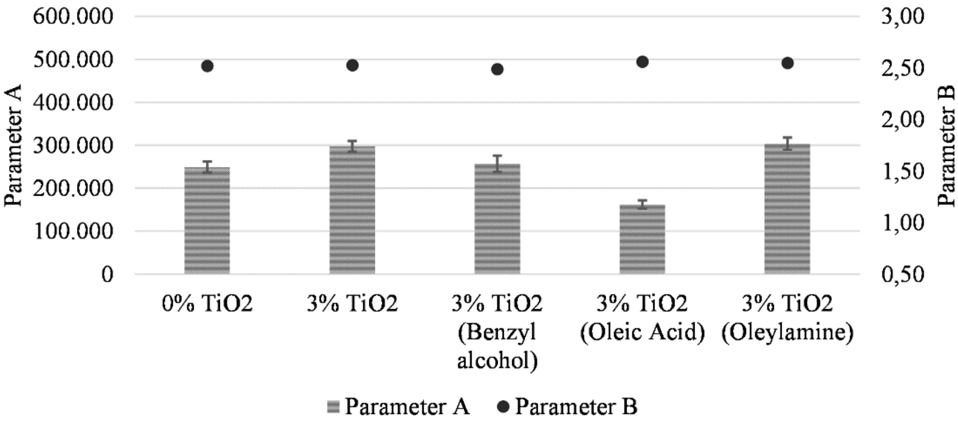

Figure 12. A and B parameters for asphalt binder 55/75 E + Nano TiO_2

Figure 14 illustrates that the Nf values of samples with oleylamine-modified titanium dioxide are higher than neat binder samples and samples with other modified nanoparticles regarding low and high strain levels. This fact indicates that adding nanoparticles modified with this agent was the most beneficial to increasing a binder's fatigue resistance.

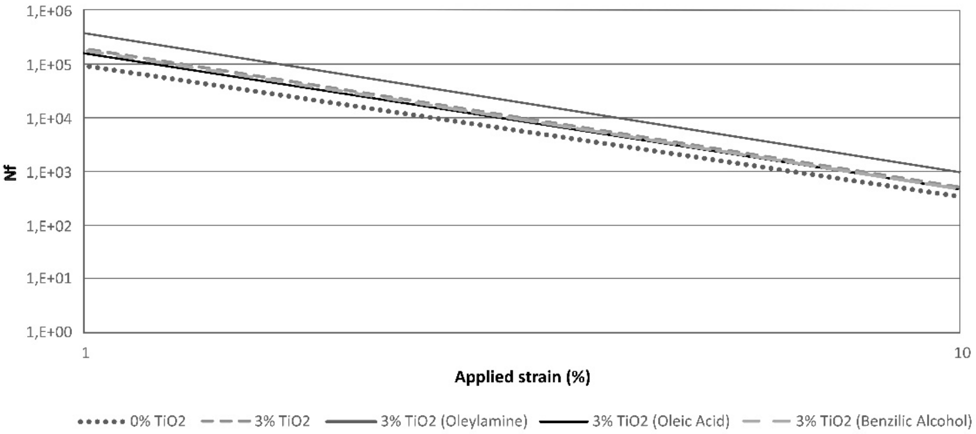

Figure 13. Number of cycles until failure for asphalt binder 50/70 + Nano TiO_2

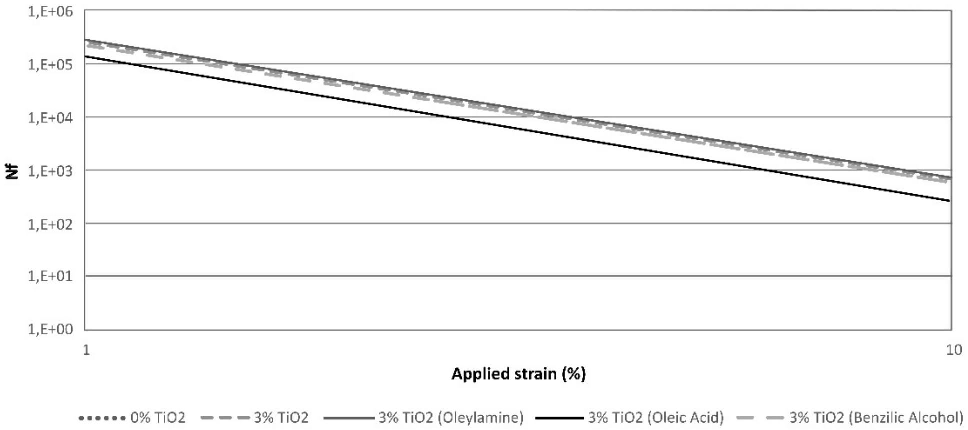

Figure 14. Number of cycles until failure for asphalt binder 55/75-E + Nano TiO_2

Considering binder 55/75-E, the curve representing the oleic acid-modified nanoparticles shows that Nf values decreased for all strain levels. The curve of benzyl alcohol-modified nanoparticles shows that the agent had practically no effect on properties related to a binder's fatigue resistance. The number of cycles of the oleylamine-modified nanoparticles curve was approximately 24% higher than the neat binders. The poor performance of the modifications may indicate that they do not affect the surface of nanoparticles, and instead of acting as dispersants, they may be acting as agglomerating agents. Therefore, they may either not affect (benzyl alcohol) or negatively (oleic acid).

Figures 15 and 16 present the shear stress versus strain data obtained from the amplitude sweep test. Figure 14 shows that all modified binders obtained higher shear stresses than the neat binder did, and the peaks were projected to the right. These facts indicate that the modified binders bear higher stresses and strains. It should also be noted that the binder with oleylamine-modified nanoparticles presents a higher peak than the binder with unmodified particles. This peak, however, is more inclined to the right, with around 15% strain, against 12% of the other contents. Therefore, this modification also increased resistance to deformation and held up the shear stress peak about the neat binder.

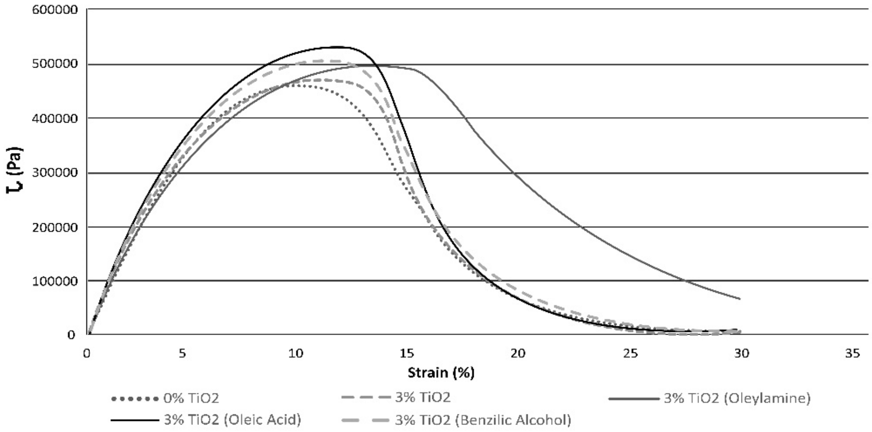

Figure 15. Stress x Strain curve for asphalt binder 50/70 + Nano TiO_2

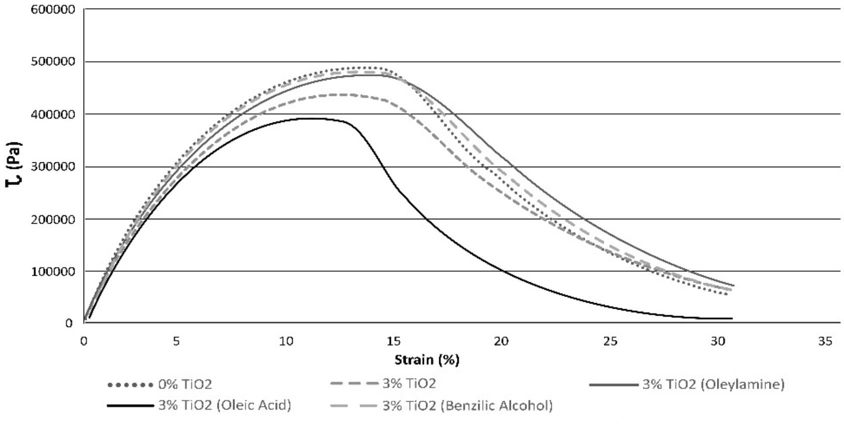

Figure 16. Stress x Strain curve for asphalt binder 55/75-E + Nano TiO_2

Figure 16 indicates that the oleic acid modifications negatively influenced the binder. They reduced its supported shear stress peak and the deformation level at which this resistance peak occurred, demonstrating that the binder became less resistant. The other modifications presented similar behavior to the unmodified binder. However, it should be noted that the oleylamine modification did not change the supported stress level for the neat binder but caused a smaller decline at the end of the curve, indicating that this binder probably supports more significant residual deformation.

For LAS analysis, Nascimento (2021) apud. Possebon (2021) presented the classification of asphalt binders called the binder fatigue factor (FFB). He based this classification on Petrobras's large volume of data on asphalt binders (Table 4).

Table 4 – FFB classification for asphalt binder by LAS analysis

Classification	FFB PSE
1 - Poor	FFB < 1,22
2 - Inferior	1,22<FFB<1,31
3 - Average	1,31<FFB<1,48
4 - Superior	1,48<FFB<1,57
5 - Excellent	FFB>1,57

Font: Nascimento (2021) apud. Possebon (2021)

Table 5 presents the results obtained for the asphalt binders studied in this research. The results obtained verified that the binders modified superficially with oleylamine for both cases reached FFB values higher than the other conditions of addition of nanoparticles.

Table 5 – Classification of ligands evaluated for FFL

Asphalt Binder	FFLPSE19°C	FFB Classification proposed by Nascimento (2021) apud. Possebon (2021)
50/70 0% TiO_2	1,358	3 - Average
50/70 3% TiO_2	1,412	3 - Average
50/70 3% TiO_2 BA	1,419	3 - Average
50/70 3% TiO_2 AO	1,411	3 - Average
50/70 3% TiO_2 OL	1,506	4 - Superior
55/75 0% TiO_2	1,487	5 - Excellent
55/75 3% TiO_2	1,464	4 - Superior
55/75 3% TiO_2 BA	1,458	4 - Superior
55/75 3% TiO_2 AO	1,419	4 - Superior
55/75 3% TiO_2 OL	1,497	5 - Excellent

4. CONCLUSION

The analysis of the FTIR spectra for the asphalt binders 50/70 and 55/75-E indicated the appearance of peaks related to the oxidation of the binders after the aging process. However, it was not possible to recognize other significant chemical differences in the ligands about the addition of TiO_2 nanoparticles.

Oleylamine and benzyl alcohol surface modifiers showed positive results for the asphalt binder 50/70 and the asphalt binder 55/75-E since those surface modifiers could delay the aging process and increase the PG. Therefore, both asphalt binders displayed the potential to withstand higher working temperatures and lower aging rates.

The non-recoverable compliance for the asphalt binder 50/70 decreased about 15% when benzyl alcohol was used as a surface modifier at low-stress level (Jnr 100 Pa^{-1}), and about 8% at high-stress levels (3200 Pa^{-1}) for benzyl alcohol and oleylamine, which allows for an improvement in that binder's resistance to permanent deformation. However, the asphalt binder 55/75-E values obtained for non-recoverable compliance did not positively impact the addition of the surface modifiers analyzed.

Linear Amplitude Sweep test results show that the use of oleic acid as a modifier surface agent negatively affected both asphalt binders because its behavior was similar to that of an agglomerating agent. Regarding the use of benzyl alcohol, there were no relevant changes when compared to the asphalt binder with no surface modification.

The results using oleylamine as a modifier agent shows increased values for parameter A, which reflects higher integrity of the material after it was subjected to induced damage, allowing a more significant number of cycles before fatigue failure. For the 50/70 asphalt binder modified only with TiO_2, there was an increase in the FFB parameter, proving to be superior to the pure binder. The FFB parameter achieved using oleylamine demonstrate the benefit of using this material in the surface modification of nanoparticles. Smaller Jnr values were obtained for the samples that used oleylamine as a surface modifier. This fact indicates less susceptibility to permanent deformation, whereas the highest values for the Nf parameter in the LAS test suggest greater fatigue life.

It is recommended that, in future works, healing tests be performed to compare the damage curing behavior of various pure and modified asphalt binders to understand the curing behavior of these materials in the fatigue modeling of asphalt paving materials.

It is important to emphasize that adding 3% oleylamine-modified Nano TiO_2 is the most effective way to incorporate titanium dioxide nanoparticles for both types of asphalt binder. However, positive results from incorporating modified nanoparticles in asphalt binder 50/70 were more prominent than those of SBS-modified asphalt binder 55/75-E. It is noteworthy that this work can be complemented by studies that seek to incorporate other contents (%) of nanoparticles and surface modification with other agents in the rheological, asphalt mixtures and chemical performance of modified binders. Higher incorporation contents can develop greater phase separation. Therefore, lower contents for incorporation in the asphalt binder are suggested.

The main changes related to aging were noticed in the PG test, where, for the modified binders after short-term aging, they presented initial stiffness superior to those of the base binder. This may indicate that the incorporation of surface-modified nanoparticles favors the reduction of the loss of volatile components. This study has gaps to be filled to understand better the chemical interactions and reactions caused by the asphalt binder modification process. As suggestions for future research, chemical analyzes complementary to FTIR spectroscopy are indicated, are indicated for binders with embedded nanoparticles with surface modification, as well as the evaluation of scanning electron microscopy (SEM) to evaluate the dispersion of materials in the asphalt matrix.

The incorporation of modifiers of this nature in the asphalt binder on industrial scales presents itself as a barrier to using this type of material in the modification of binders. However, the storage stability test is an essential initial step in verifying the phase separation of the material and, associated with the suggestions proposed in these conclusions, can support future work to overcome such limitations.

The performance of asphalt mixtures with these materials can allow a complementary understanding of the mechanical influence concerning fatigue and permanent deformation parameters for modified binders.

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REFERENCES

AASHTO (2010) *M 320-10: Standard Specification for: Performance-Graded Asphalt Binder*. Washington, D.C.: American Association of State Highway and Transportation Officials.

AASHTO (2012) *TP 101: Standard Method of Test for Estimating Fatigue Resistance of Asphalt Binders Using the Linear Amplitude Sweep.* Washington, D.C.: American Association of State Highway and Transportation Officials.

AASHTO (2021) *M 332: Standard Specification for Performance-Graded Asphalt Binder Using Multiple Stress Creep Recovery (MSCR) Test.* Washington, D.C.: American Association of State Highway and Transportation Officials.

Alcântara, G. B. (2007) *Nanopartículas de maguemita complexadas com ácido oleico.* Dissertation (Master in Physics). IF - Programa de Pós-Graduação, Universidade de Brasília. Brasília. Available at: https://repositorio.unb.br/handle/10482/1459 (Accessed: 01 Jul 2022).

ASTM (2006) *D36: Standard Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus).* West Conshohocken: American Society for Testing and Materials.

ASTM (2013) *D5: Standard Test Method for Penetration of Bituminous Materials.* West Conshohocken: American Society for Testing and Materials.

ASTM (2015a) *D4402: Standard Test Method for Viscosity Determination of Asphalt at Elevated Temperatures Using a Rotational Viscometer.* West Conshohocken: American Society for Testing and Materials.

ASTM (2015b) *D7405-15: Standard Test Method for Multiple Stress Creep and Recovery (MSCR) of Asphalt Binder Using a Dynamic Shear Rheometer.* West Conshohocken: American Society for Testing and Materials.

ASTM (2016) *D6373: Standard Specification for Performance-Graded Asphalt Binder.* West Conshohocken: American Society for Testing and Materials.

ASTM (2018) *D6084: Standard Test Method for Elastic Recovery of Asphalt Materials by Ductilometer.* West Conshohocken: American Society for Testing and Materials.

Beck Júnior, W. (2011) *Nanopartículas magnéticas metálicas recobertas com óxido de ferro: intensificação das propriedades magnéticas da nanopartícula e funcionalização para aplicação em biomedicina.* Dissertation (Master in Science). Instituto de Química de São Carlos, Universidade de São Paulo. São Carlos. DOI: 10.11606/d.75.2011.tde-02052011-144102.

Faruk, A. N. M. et al. (2014) “Application of Nano-Technology in Pavement Engineering: A Literature Review” in *Application of Nanotechnology in Pavements, Geological Disasters, and Foundation Settlement Control Technology*. American Society of Civil Engineers, pp. 9–16. DOI: 10.1061/9780784478448.002.

Golestani, B. et al. (2015) “Nanoclay application to asphalt concrete: Characterization of polymer and linear nanocomposite-modified asphalt binder and mixture” *Construction and Building Materials*, 91, pp. 32–38. DOI: 10.1016/j.conbuildmat.2015.05.019.

Hassan, M. M. et al. (2012) “Laboratory Evaluation of Environmental Performance of Photocatalytic Titanium Dioxide Warm-Mix Asphalt Pavements” *Journal of Materials in Civil Engineering*, 24(5), pp. 599–605. DOI: 10.1061/(asce)mt.1943-5533.0000408.

Hintz, C. and Bahia, H. (2013) “Simplification of Linear Amplitude Sweep Test and Specification Parameter” *Transportation Research Record*, 2370(1), pp. 99–106. DOI: 10.3141/2370-02.

Hong, R. Y. et al. (2009) “Synthesis, surface modification and photocatalytic property of ZnO nanoparticles” *Powder Technology*, 189(3), pp. 426–432. DOI: 10.1016/j.powtec.2008.07.004.

Johnson, C. M. and Bahia, H. U. (2010) “Evaluation of an Accelerated Procedure for Fatigue Characterization of Asphalt Binders” *Road Materials and Pavement Design*. Available at: https://uwmarc.wisc.edu/files/linearamplitudesweep/RMPD10_LAS_CMJ_HB-100321.pdf (Accessed: 01 Jul 2022).

Li, G.-Y. et al. (2008) “Preparation and properties of magnetic Fe_3O_4–chitosan nanoparticles” *Journal of Alloys and Compounds*, 466(1–2), pp. 451–456. DOI: 10.1016/j.jallcom.2007.11.100.

Li, R. et al. (2017) “Developments of nano materials and technologies on asphalt materials – A review” *Construction and Building Materials*, 143, pp. 633–648. DOI: 10.1016/j.conbuildmat.2017.03.158.

Magalhães, M. J. M. (2014) *Síntese e modificação da superfície de nanocristais semicondutores para aplicação como sondas fluorescentes em meio não-aquoso*. Dissertation (Master in Quality Control). Faculdade de Farmácia, Universidade do Porto. Porto. Available at: https://repositorio-aberto.up.pt/bitstream/10216/77261/2/33381.pdf (Accessed: 01 Jul 2022).

Mahali, I. and Sahoo, U. C. (2019) “Rheological characterization of Nanocomposite modified asphalt binder” *International Journal of Pavement Research and Technology*, 12(6), pp. 589–594. DOI: 10.1007/s42947-019-0070-8.

Marinho Filho, P. G. T. (2017) *Avaliação reológica de ligantes asfálticos modificados com nanopartículas de dióxido de titânio.* Dissertation (Master in Civil and Environmental Engineering). Programa de Pós-Graduação em Engenharia Civil e Ambiental, Universidade Federal de Campina Grande. Campina Grande. Available at: http://dspace.sti.ufcg.edu.br:8080/jspui/handle/riufcg/374 (Accessed: 01 Jul 2022).

Medeiros, I. A. F. de (2018) *Nanoestruturação de Ferritas de Cobalto (CoxFe3-xO4): efeito sobre a catálise e sobre a detecção de gases poluentes.* Thesis (PhD in Chemical Engineering). Programa de Pós-Graduação em Engenharia Química, Universidade Federal do Rio Grande do Norte. Natal. Available at: https://repositorio.ufrn.br/jspui/handle/123456789/26212 (Accessed: 01 Jul 2022).

Mourdikoudis, S. and Liz-Marzán, L. M. (2013) “Oleylamine in Nanoparticle Synthesis” *Chemistry of Materials*. American Chemical Society, 25(9), pp. 1465–1476. DOI: 10.1021/cm4000476.

NCHRP (2001) *Report 459 - Characterization of Modified Asphalt Binders in Superpave Mix Design*. Washington, D.C.: National Cooperative Highway Research Program.

Olsen, R. E. (2013) *Synthesis, characterization, and application of high surface area, mesoporous, stabilized anatase TiO2 catalyst supports.* Dissertation (Doctor of Philosophy). Department of Chemistry and Biochemistry, Brigham Young University. Provo. Available at: http://hdl.lib.byu.edu/1877/etd6632 (Accessed: 01 Jul 2022).

Possebon, É. P. (2021) *Caracterização avançada de ligantes e misturas asfálticas brasileiras*. Thesis (PhD in Civil Engineering). Programa de Pós-Graduação em Engenharia Civil, Universidade Federal de Santa Maria. Santa Maria. Available at: http://repositorio.ufsm.br/handle/1/22487 (Accessed: 01 Jul 2022).

Rong, M. Z., Zhang, M. Q. and Ruan, W. H. (2006) "Surface modification of nanoscale fillers for improving properties of polymer nanocomposites: a review" *Materials Science and Technology*, 22(7), pp. 787–796. DOI: 10.1179/174328406x101247.

Shafabakhsh, G., Mirabdolazimi, S. M. and Sadeghnejad, M. (2014) "Evaluation the effect of nano-TiO_2 on the rutting and fatigue behavior of asphalt mixtures" *Construction and Building Materials*, 54, pp. 566–571. DOI: 10.1016/j.conbuildmat.2013.12.064.

Sobreiro, F. P. (2015) *Efeito da adição de ácidos fosfóricos no comportamento reológico de ligantes asfálticos puros e modificados com copolímero SBS.* Thesis (PhD in Science). Escola de Engenharia de São Carlos, Universidade de São Paulo. São Carlos. DOI: 10.11606/t.18.2014.tde-28052014-100359.

Sousa Neto, V. F. de (2019) Avaliação reológica do ligante asfáltico modificado com nanopartículas de óxido de zinco. Dissertation (Master in Civil and Environmental Engineering). Programa de Pós-Graduação em Engenharia Civil e Ambiental, Universidade Federal de Campina Grande. Campina Grande. Available at: http://dspace.sti.ufcg.edu.br:8080/jspui/handle/riufcg/3342 (Accessed: 01 Jul 2022).

Tanzadeh, J. et al. (2012) "Laboratory Study on the Effect of Nano TiO_2 on Rutting Performance of Asphalt Pavements" *Advanced Materials Research*, 622–623, pp. 990–994. DOI: 10.4028/www.scientific.net/amr.622-623.990.

Viali, W. R. (2009) *Síntese e Caracterização de nanopartículas de maghemita revestidas com ácido oléico para obtenção de fluidos magnéticos a base de óleos isolantes.* Dissertation (Master in chemistry). Instituto de Química, Universidade Federal de Goiás. Goiânia. Available at: http://repositorio.bc.ufg.br/tede/handle/tde/1059 (Accessed: 01 Jul 2022).

Wang, L. S. and Hong, R. Y. (2011) "Synthesis, Surface Modification and Characterisation of Nanoparticles", in B. Reddy (ed.), *Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications*, IntechOpen, London. DOI: 10.5772/10540.

Yang, S. et al. (2018) "Ultraviolet and PAV aging procedures influence on rheological characteristics of Sasobit/SBS modified binder containing titanium dioxide nanoparticles" *Petroleum Science and Technology*, 36(19), pp. 1524–1530. DOI: 10.1080/10916466.2018.1476535.

You, L. et al. (2018) "Assessment of nanoparticles dispersion in asphalt during bubble escaping and bursting: Nano hydrated lime modified foamed asphalt" *Construction and Building Materials*, 184, pp. 391–399. DOI: 10.1016/j.conbuildmat.2018.06.234.

You, Z. et al. (2011) "Nanoclay-modified asphalt materials: Preparation and characterization" *Construction and Building Materials*, 25(2), pp. 1072–1078. DOI: 10.1016/j.conbuildmat.2010.06.070.

Zhang, H. et al. (2015) "Influence of surface modification on physical and ultraviolet aging resistance of bitumen containing inorganic nanoparticles" *Construction and Building Materials*, 98, pp. 735–740. DOI: 10.1016/j.conbuildmat.2015.08.138.