Artículo Original

Rheological properties of asphalt binders modified with montmorillonite

Loredanna Melyssa Costa de Souza[1], Ana Maria Gonçalves Duarte Mendonça[1], Osires de Medeiros Melo Neto[1,*], John Kennedy Guedes Rodrigues[1], Robson Kel Batista de Lima[1]
[1]Department of Civil Engineering, Federal University of Campina Grande, Aprígio Veloso 882, 58428-830 Campina Grande, Brazil.
*Autor de correspondencia: osiresdemedeiros@servidor.uepb.edu.br

Abstract

Modification techniques for asphalt binders, polymers, fillers, fibers, and recently nanomaterials have been used to improve the performance of asphalt mixtures. This study evaluated the effect of incorporating pure clay nanoparticles, modified by stearyl dimethyl ammonium chloride (Praepagen WB) and cetyl trimethyl ammonium chloride (Genamin) in the contents of 2, 3, 4, and 5% to petroleum asphalt cement with 50/70 degrees of penetration. Physical and rheological tests analyzed the binders: penetration, softening point, rotational viscosity, degree of performance; these tests were performed before and after the short-term aging procedure and the creep and recovery under multiple stress procedures. The results showed that these modifiers increased the softening point and viscosity, decreased penetration and improved permanent deformation. The contents used in this research did not show a significant increase in mixing temperatures. In addition, the modifiers showed antioxidant properties. Overall, the organophilic Montmorillonite WB had the best results in the tests performed. It was concluded that the use of Montmorillonite as a modifier of the asphalt binder is an effective method to improve the properties of the binder.

Keywords: asphalt binder, nanoparticles, montmorillonite, praepagen WB, genamin

1. Introduction

Asphalt binder is a viscoelastic material whose temperature sensitivity and aging susceptibility are intrinsic characteristics. These properties make the asphalt pavement naturally influenced by environmental factors [1-3]. In regions with a humid climate, the dynamic load of traffic transmits moisture in the pavement layers, creating water pressure in the pores and possibly causing wear due to fatigue and permanent deformation [4, 5]. The asphalt binder is susceptible to temperature, permanent deformation at high temperatures, and cracking at low temperatures [6, 7].

The search for materials that provide improved asphalt pavement performance has gained considerable visibility recently [8, 9]. As a result, research using nanomaterials has become widespread in recent years [10-13]. Nanomaterials have a high surface area and tiny sizes compared to other additives used in asphalt binders. These characteristics are considered special and unique for hot asphalt mixes [14, 15]. Among the nanomaterials used to improve the properties of asphalt mixtures, nanoclay has attracted attention to researchers in pavement research [16].

Nano-zinc oxide and organically expanded vermiculite were evaluated through rheological tests on asphalt binders before and after aging. It was concluded that adding this modifier improves the resistance to permanent deformation and thermal oxidation and the antiaging action of the asphalt binder [17]. Wang, Zhang, and Zhu [18] evaluated the effect of multiscale nano-composites on asphalt binder performance. Organically expanded vermiculite mixed with nano-TiO_2, nano-ZnO, and nano-SiO_2 was used to form multiscale nano-composites, and it was found that the use of multiscale nanomaterials has adverse effects on high-temperature properties. However, they increased indirect tensile strength at low temperatures and positively affected fatigue and antiaging performance.

The influence of nanoclay and nano-composites on the rheological properties of the asphalt binder was studied by Farias *et al.* [19]. The organophilic montmorillonite clay was prepared to be used as an additive for a pure and polymer-modified asphalt binder. Among the types evaluated, montmorillonite with polymer-modified binder showed the best resistance to permanent deformation and elastic recovery.

Nanoclay-modified asphalt binder was studied by Ezzat *et al.* [10] and found that nanoclay at 3% by weight of the binder improved its performance. The modified binder is more suitable for hot climate regions, and the results showed lower penetration value, increased softening point temperature, and increased viscosity. However, percentages above 3% had an adverse effect.

Vargas *et al.* [20] evaluated the effects of montmorillonite and two different organic additives on asphalt binder performance. Pure montmorillonite, modified with trimethyloctadecacyl ammonium chloride and modified with aminopropyl-triethoxysilane, were rheologically analyzed, and the authors concluded that the addition of nanoclay to the asphalt decreases penetration and increases the softening point and viscosity. In addition, the modified binders showed higher complex modulus, lower phase angle, and higher resistance to permanent deformation. The montmorillonite modified with trimethyloctadecacyl ammonium chloride showed better results in physical properties and resistance to permanent deformation.

Mortezaei *et al.* [13] studied the effects of premix on the rheological characteristics of asphalt binder modified with clay nano-composites and styrene-butadiene-styrene (SBS) polymer. The nanoclay used was the organophilic montmorillonota (OMMT) type, Cloisite 15A, and the SBS was the SBS 501LG type. The research showed better results with the realization of the premix and exemplary performance in rheological properties using these additives.

A study evaluated the resistance to permanent deformation, fatigue, and temperature susceptibility of the asphalt rubber binder modified with nanoclay. The results showed that the addition of nanoclay improved the rheological properties of the rubber asphalt binder, reducing permanent deformation, increasing fatigue resistance, and elastic recovery [21].

Thus, the following question arises: What is the effect of adding organophilic montmorillonite compared to incorporating pure montmorillonite into the asphalt binder? This research evaluates the physical and rheological performance of asphalt binder with 50/70 degree of penetration modified by organophilic montmorillonite compared to the binder modified by pure montmorillonite.

2. Materials and Methods

This section describes the materials and test procedures performed during the experimental phase of the research, performed according to American Society for Testing and Materials (ASTM) and the American Association of State Highway and Transportation Officials (AASHTO).

2.1 Materials

The modified asphalt binder used has a 50/70 degree of penetration (PAC 50/70). The choice of this asphalt binder is due to its wide use in Brazil, the country where the research was conducted. The pure clay montmorillonite sodica (MMT) used in the research was supplied by Indústria Bentonit União Nordeste (BUN), located in the city Campina Grande-PB.

The modification process was based on the studies by Mortezaei *et al.* [13] and Vargas *et al.* [20], who used organic modifiers on montmorillonite. To make the clays more compatible with the SBS polymer, sodium ions were exchanged for ammonium ions. This exchange was carried out in the presence of two distinct quaternary ammonium salts: Praepagen WB - stearyl dimethyl ammonium chloride (WB) and Genamim CTAC-50ET® - cetyl trimethyl ammonium chloride (GNM), produced by VETEC - São Paulo/S.P.

The preparation of organophilic clay treated with Praepagen WB and Genamin salts is similar. Therefore, dispersions containing 768 ml of distilled water and 32 g of clay were prepared. The clay was added little by little with concomitant mechanical agitation and kept for 20 minutes. Then, a solution containing distilled water and the quaternary ammonium salt (Praepagen WB or Genamim) was added. Stirring was continued for another 20 minutes. Then, the containers were closed and kept at room temperature for 24 hours. After that time, the material obtained was filtered to remove excess salt. Washing was carried out with approximately 2000 ml of distilled water using a Buchner Funnel with a kitassate, coupled to a vacuum pump. The agglomerates obtained were dried in an oven at 60°C ± 5°C for 48 hours. Finally, the already dried agglomerates were disaggregated and passed through an ABNT nº 325 sieve (diameter = 0.044 mm) to be further characterized. Table 1 presents the nomenclatures of the samples used.

Table 1. Sample nomenclature

Samples	**Nomenclature**
Petroleum Asphalt Cement with 50/70 degree of penetration	PAC 50/70
PAC 50/70 + 2% Montmorillonite	2% MMT
PAC 50/70 + 3% Montmorillonite	3% MMT
PAC 50/70 + 4% Montmorillonite	4% MMT
PAC 50/70 + 5% Montmorillonite	5% MMT
PAC 50/70 + 2% Organophilized Montmorillonite with Genamin	2% OMMT-GNM
PAC 50/70 + 3% Organophilized Montmorillonite with Genamin	3% OMMT-GNM
PAC 50/70 + 4% Organophilized Montmorillonite with Genamin	4% OMMT-GNM
PAC 50/70 + 5% Montmorillonite Organophilized with Genamin	5% OMMT-GNM
PAC 50/70 + 2% Montmorillonite Organophilized with Praepagen WB	2% OMMT -WB
PAC 50/70 + 3% Montmorillonite Organophilized with Praepagen WB	3% OMMT -WB
PAC 50/70 + 4% Montmorillonite Organophilized with Praepagen WB	4% OMMT -WB
PAC 50/70 + 5% Montmorillonite Organophilized with Praepagen WB	5% OMMT -WB

2.2 Methods

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

To obtain the modification of the binder, the mixture of materials consisted of adding to the PAC 50/70 the contents of 2, 3, 4, and 5% of pure montmorillonite and organophilic montmorillonite with the salt Praepagen WB and Genamin. A low-shear mechanical stirrer was used to modify the binder, which applies rotating movements through a 10 cm diameter helix. The sample was placed in a glass beaker with a capacity of 3 liters. The beaker is wrapped in a thermal blanket to maintain the desired temperature of agitation. The equipment shows a rotation speed and also has a device that regulates the temperature.

Through tests using the mechanical stirrer with PAC samples, it was possible to obtain values related to mixing time and rotation used in the research. For all the modifications, the rotation was around 400 rpm, a maximum rotation reached by the stirrer without any loss of material. The time was determined when the PAC + montmorillonite mixture visibly presented the absence of lumps and homogeneity, establishing a time of 30 minutes. Jahromi and Khodaii [22] pointed out in their work that the binder modification was carried out in a mechanical stirrer, with a speed of 550 rpm and lasting for 30 minutes.

So that the temperature of the PAC and modifier mixture remained constant during the time established in the mechanical stirrer, a lid was placed under the beaker so that during the modification, there were no significant changes in temperature, keeping it at (150 ± 5) °C.

After obtaining the modified asphalt binders, the physical and rheological characterization of the binders was carried out, before and after the Rolling Thin Film Oven (RTFO) aging procedure ASTM D2872 (2019), through the Penetration tests ASTM D5M:2020, Softening Point ASTM D36M-14:2020, Rotational Viscosity ASTM D4402:2020, Performance Grade (PG) ASTM D6373:2021 and Multiple Stress Creep Recovery (MSCR) ASTM D7405:2020.

3. Results and Discussions

In this topic, the results obtained in the experimental phase of asphalt binders modified by the addition of montmorillonite are presented and discussed.

3.1 Physical characterization

Table 2 presents the results of the physical characterizations for the samples analyzed in this research. It is observed that the modified binders, in all contents, showed a decrease in penetration values before RTFO conditioning when compared to PAC 50/70. After RTFO, the trend was to reduce penetration for most samples, except samples with 4% MMT and 5% MMT. The most significant reduction in penetration value compared to PAC 50/70, before and after RTFO, was the sample with 2% MMT, which showed a reduction of 60.66% before aging and 72.57% after short-term aging. Thus, the addition of montmorillonite leads to a gain in stiffness to the asphalt binder both before and after aging, especially for the sample with 2% MMT.

Shafabakhsh and Ani [23], Ali *et al.* [24], Sun *et al.* [25], and Melo Neto *et al.* [26] state that it is common to reduce penetration as fractional particles are added to asphalt binders. Marinho Filho [27] shows a similar result in his study when adding fractional particles of titanium dioxide (TiO_2). The DNIT 095-EM:2006 Standard establishes limits for the results of this test for different types of asphalt binders. For the asphalt binder PAC 50/70, the penetration ranges are between 50 and 70 dmm. Therefore, it was possible to analyze that the test results are within the acceptable range.

It is known that the binder is more rigid after short-term aging, which did not occur with the samples modified by MMT, which showed a slight increase in the penetration value when compared to the results before RTFO. What can also be observed is that the addition of the contents caused an increase in penetration compared to the previous content, both before and after aging, which demonstrates that the addition of a more significant amount of montmorillonite provides a lower stiffness to the binder in the mixture.

Table 2. Physical characterization before and after RTFO of pure and modified asphalt binders

Test Samples	Penetration 0.1 mm (100g, 5s a 25°C)	Softening Point (°C)	Rotational Viscosity (cP)		
			135 °C	150°C	177 °C
Tests Before RTFO					
PAC 50/70	54.4	48	377.5	186.5	68.25
2% MMT	33	52.5	411.3	203	72.3
3% MMT	37.8	50.75	418.8	206	73.5
4% MMT	47	48	427.5	211.5	74.25
5% MMT	49.2	45.5	431.8	211	75
2% OMMT-WB	43.2	54.6	438.8	215.5	76.25
3% OMMT-WB	41.7	54	455	223.5	78.25
4% OMMT-WB	41	54	483.8	236	83
5% OMMT-WB	39.8	52	485	247	86.25
2% OMMT-GNM	48	51	447.5	218.5	77
3% OMMT-GNM	44	53	482.5	234	82
4% OMMT-GNM	42	53	538.8	262.5	89.75
5% OMMT-GNM	42	51	575	278	95.75
Tests After RTFO					
PAC 50/70	47.4	52	520	284.5	85.5
2% MMT	34.4	55	582.5	275	93.25
3% MMT	44.6	53	533.8	255	87.75
4% MMT	48.3	49	537.5	267.5	89.3
5% MMT	51	49	548.8	274.3	92
2% OMMT-WB	39.5	56	558.8	276	89
3% OMMT-WB	40	56	563	273.5	88.25
4% OMMT-WB	37.3	55	583	280.8	93.75
5% OMMT-WB	37	55	585.3	281	95
2% OMMT-GNM	45	54	595	282.5	96.25
3% OMMT-GNM	43	54	662.5	299	100.5
4% OMMT-GNM	40	55	715	341	115.3
5% OMMT-GNM	39	54	747.5	354.5	119.5

Ezzat *et al.* [10] observed in their study with clay nanoparticles that the presence in the asphalt binder improves the penetration rate; as the percentage of the modifier increases, there is a linear decrease in penetration up to 5% of this additive. In the research by Melo [28], the incorporation of clay in the PAC 50/70, at levels 1, 2, and 3% of modification, caused a reduction in penetration after aging, a reduction also observed in the research by Jahromi and Khodaii [22], who studied the incorporation of clay cloisite 15-A, for the pure and modified binder with contents of 2%, 4%, and 7%, and presented penetration of 62 dmm, 56 dmm, 53 dmm, and 42 dmm, respectively. Tomé [29] modified the PAC 50/70 with 4% OMMT and observed an increase in the consistency of the binder, with a decrease in penetration values and the results found in this research.

The Retained Penetration is data used to analyze the sensitivity of the binder to oxidation, which indicates the capacity of a binder to maintain its penetration characteristics after aging. According to National Agency for Petroleum, Natural Gas and Biofuels, for an asphalt binder PAC 50/70 subjected to short-term aging in the RTFO, a minimum of 55% of retained penetration is admitted. Fig. 1 shows the retained penetration of the tested samples.

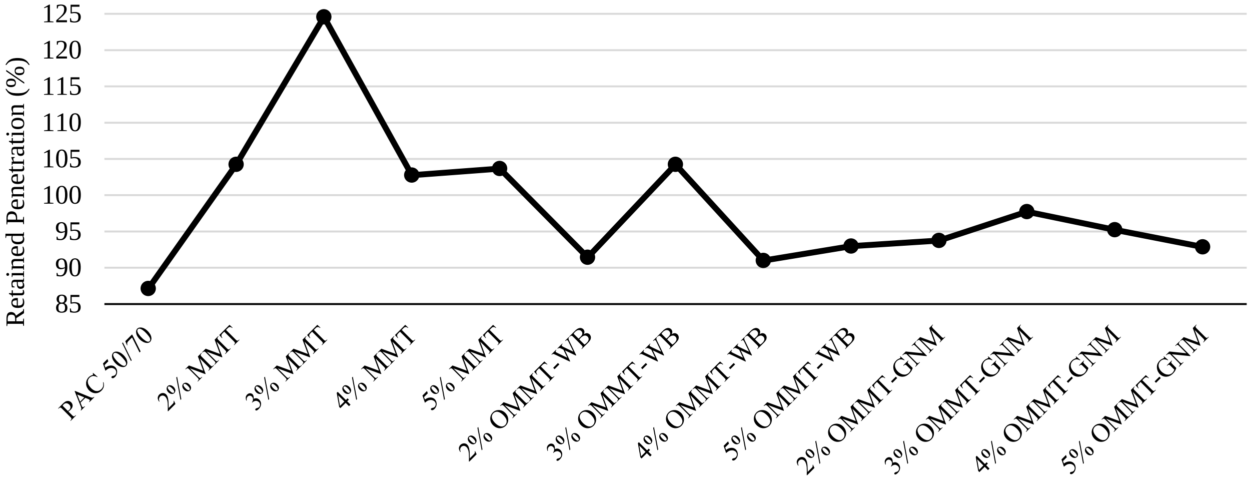

Fig.1 Retained Penetration of Samples

Therefore, it is observed that the results are following the specified. Furthermore, it is possible to observe that the binder modification by OMMT-GNM, MMT, and OMMT-WB increased the Retained Penetration value, showing more excellent resistance to aging. Furthermore, the results found between the modification contents of the binder showed slight variation, indicating that there is a stabilization of the material regarding the contents used.

The softening point is related to the maintenance of the properties of the binder at high temperatures and the increase in resistance to permanent deformation [25]. This parameter was obtained from the average of the two test temperatures. As expected, the results showed an increase in the softening point in the binder modified with Genamin compared to the pure binder before and after aging. Before the aging test, a softening point of 48°C was found for PAC 50/70, and binders with contents of 2, 3, 4 and 5%, the flow temperature was 51°C, 53° C, 53°C and 51°C, respectively, with 5°C being the most significant increase found, for the content of 2% OMMT-GNM and 5%OMMT-GNM, concerning PAC 50/70. After aging, a temperature of 52°C was found for the pure binder and 54°C for the binders with contents of 2%, 3%, and 5%, and 55°C for the binder with 4% OMMT-GNM, being this is the binder that showed the most significant increase about the softening point of PAC 50/70. These results corroborate Ezzat *et al.* [10], who pointed out in their study that nanoclay increased the softening point in samples with up to 3% addition of this modifier, then the values decreased slightly afterward.

The modification of the binder by organophilic montmorillonite with Genamin caused an increase in the minimum flow temperature, which is a result that was also found in the studies by Melo [28] and Tomé [29], in which an increase in temperature was observed, consequently, increase its softening point. Researchers Jahromi and Kodaii [22] also studied the effects of montmorillonite on the physical and rheological properties of the binder modified with the organophilic montmorillonite Cloisite – 15A, with contents of 2%, 4%, and 7%, when performing the Point of Point test. Softening was verified an increase in temperature concerning the pure PAC as the modification contents increased, having approximately the following results: for the PAC 50/70, a temperature of 54°C, and the contents of 2, 4, and 7%, the flow temperatures were 55.5°C, 56.5°C, and 62°C, respectively.

Concerning the variation of the softening point, for the PAC 50/70, the maximum allowed increase is 8°C, according to the norm DNIT 095-EM:2006; therefore, the studied samples fulfill these recommendations. A decrease in the softening point may indicate minor aging of the asphalt binder, as the softening point is related to the material's stiffness. Asphalt binders after the aging procedure have greater stiffness and, therefore, have softening point values [26].

The results indicated that the samples modified with montmorillonite organophilic with Genamin had a lower softening point variation. This proves that the addition of montmorillonite delayed the effect of oxidation and volatilization produced by the conditioning of RTFO. On the other hand, the reference samples showed the highest variation values, confirming their susceptibility to the aging phenomenon. It is noteworthy that among the samples modified with OMMT-GNM, the one with the lowest softening point variation was the sample modified with 3% OMMT-GNM, however with a value very close to the sample modified with 4% OMMT-GNM. Considering that the modified samples did not present a modification saturation point until the present result, the different ranges of 3 and 4% should be better evaluated for possible saturation observation.

High values of Softening Point variation indicate a greater sensitivity of the binder to aging in the short term, so PAC 50/70 is the one with the most significant variation, corroborating the results obtained for penetration. An increase in the softening point results in a lesser sensitivity of the binder to temperature variation and more excellent resistance to plastic deformation.

The thermal susceptibility index (TSI) is another parameter that can be evaluated from the penetration and softening point results (Equation 1). This parameter indicates the sensitivity of the consistency of asphalt binders to temperature variation. According to Ehinola *et al.* [30], TSI values can vary between -4 for high susceptibility index and +6 for low thermal susceptibility index, where the higher the TSI value, the lower the thermal susceptibility of the binder, i.e., less sensitive to temperature variation. Table 3 presents the thermal susceptibility indices for pure and modified binders.

$$TSI = \frac{(500)(logPEN)+(20)(T°C)-1951}{120-(50)(logPEN)+(T°C)} \tag{1}$$

T°C = Softening point

PEN = Penetration 0.1 mm (100 g, 5 s a 25 °C)

Table 3. Binder thermal susceptibility indices

Test Samples	**TSI**
PAC 50/70	-1.65
2% OMMT-GNM	-1.04
3% OMMT-GNM	-0.88
4% OMMT-GNM	-0.86
5% OMMT-GNM	-1.38
2% MMT	-1.47
3% MMT	-1.6
4% MMT	-1.84
5% MMT	-2.41
2% OMMT-WB	-0.44
3% OMMT-WB	-0.66
4% OMMT-WB	-0.81
5% OMMT-WB	-1.21

The proximity of the results was observed for the samples modified with 3 and 4%, and a subsequent increase in the result for modified content with 5%. As mentioned before, the modification range of 3 and 4% indicate a change in the behavior of the modified mixtures indicating a saturation.

It is pointed out that the binder modified by OMMT-WB has lower thermal susceptibility, indicating that the addition of montmorillonite praepagen WB reduces its sensitivity to aging, which corroborates the studies by Melo [28], in which the addition of this material in the binder pure decreased the thermal susceptibility index (TSI). The results were consistent as Bernucci *et al.* [31] says that if the TSI is greater than +1, it indicates an oxidized ligand, not very sensitive to high temperatures and becomes brittle at lower temperatures. Thus, considering that montmorillonite is a non-reactive compound to the asphalt binder, it maintains a good part of the original properties of the reference binder. However, it is worth noting that the samples modified with the OMMT-WB were less susceptible to thermal variation when compared to the PAC 50/70 sample.

In general, the modification of asphalt binders causes an increase in the binder viscosity, which is consequently associated with the mixing and compaction temperatures, which suffer an increase in their value due to the use of the modifier. However, the increase in this viscosity is related to the type and proportion of the incorporated modifier and its interaction with the base binder. The binder with the lowest viscosity value was PAC 50/70. The addition of modifying agents increased the viscosity value of the tested samples, thus decreasing the fluidity (or increasing the stiffness) of the tested samples.

Samples modified with MMT produced minor viscosity increases. However, even with the trend of increasing viscosity already mentioned, the results found for the samples modified with MMT were close to each other. Thus, they indicated that asphalt mixtures produced by these contents would present similar mixing and compaction temperatures. Another point is that even the highest MMT addition content, the 5% content, presented viscosity values lower than the values obtained for the other modifiers.

Samples modified with WB followed the same trend of increasing viscosity with the increasing proportion of the modifying agent. However, there is a more significant gain in viscosity values of this material when compared to samples modified with MMT. Another fact to be observed is the more significant variation in viscosity values regarding the proportion of WB. While the samples added with MMT showed slight variation in viscosity values concerning the proportion of MMT, the samples modified with WB varied significantly among themselves. The same behavior was observed with the samples modified with GNM, wherein the contents of 3 and 4%, there is a greater variation in viscosity values than the other samples' results. This variation may indicate the saturation content of montmorillonite in the binder, showing that for contents above 4%, the binder begins to show a mischaracterization of its properties.

Gama [32] and Mendonça *et al.* [33] explains that the increase in viscosity is related to the increase in asphaltenes in the binder. As the increase in stiffness is also associated with the increase in asphaltenes, it is possible to state that the increase in viscosity is related to the increase in the stiffness of the asphalt binder. Ezzat *et al.* [10] pointed out in their study that the 3% nanoclay modifier provided an increase in the viscosity of the asphalt binder, and at 7%, it decreased the viscosity. Farias *et al.* [19] and Melo Neto *et al.* [26] also show in their research results that the addition of nanoparticles leads to an increase in viscosity.

The ideal viscosity for the mixture allows the asphalt binder to involve all the aggregates, according to the Superpave asphalt mixture design manual [34]. Excessively high viscosities can cause the uneven coating of the aggregate. On the other hand, very low viscosities can lead to slippage of the asphalt mixture when compacted by the action of compaction rollers [32]. Therefore, it is essential to determine the Mixing temperature (MT) and Compaction Temperature (CT).

Bernucci *et al.* [31] point out that the ideal temperature of the PAC for carrying out the asphalt mixture should be situated at 0.17±0.02 Pa.s when measured with a rotational viscometer. Given the results obtained with the rotational viscosity, it was possible to analyze the mixing and compaction temperatures of the tested samples. Table 4 presents the results obtained.

Table 4. Mixing and Compaction Temperature

Sample	Mixing Temperature (°C)	Compaction Temperature (°C)
PAC 50/70	153 ± 3	139 ± 3
2% MMT	155 ± 3	141 ± 3
3% MMT	155 ± 3	141 ± 3
4% MMT	156 ± 3	142 ± 3
5% MMT	156 ± 3	142 ± 3
2% OMMT-WB	157 ± 3	143 ± 3
3% OMMT-WB	157 ± 3	144 ± 3
4% OMMT-WB	159 ± 3	145 ± 3
5%OMMT-WB	157 ± 3	143 ± 3
2% OMMT-GNM	157 ± 3	143 ± 3
3% OMMT-GNM	159 ± 3	145 ± 3
4% OMMT-GNM	161 ± 3	148 ± 3
5% OMMT-GNM	162 ± 3	150 ± 3

It is possible to observe that the increased temperature obtained by the samples modified with MMT is small, if not irrelevant, considering that the temperature ranges are very close. When analyzing the other samples, it is observed that even being above the temperature range for the PAC 50/70, this variation is also not high. The most significant mixing and compaction temperatures variation occur in the sample 5% OMMT-GNM, 9°C, and 11°C, respectively. Even though it is not high, this variation must be considered, as it is directly linked to the costs of producing asphalt mixtures and the emission of harmful gases.

3.2 Rheological Analysis

The degree of performance (PG) of the samples tested before and after short term aging (RTFO) did not vary for the samples tested. The Maximum Degree of Performance (PG) temperature for the asphalt binders under study was 64 °C. The favorable fact is that, when analyzing the $G^*/\sin\delta$ parameters, there was no degradation in the quality of the asphalt binder with the modifying agents; that is, they did not suffer from the oxidation effect at the high application temperatures, but no benefit was added to the binder asphalt. Furthermore, it is noted that the addition of the contents did not change the maximum PG temperatures before and after short-term aging (RTFO), concluding that there are no changes in the binder properties, keeping the PG temperature constant, resistant to the oxidative effect, maintaining the properties of deformability and rigidity at high temperatures. Ezzat *et al.* [10] proved in their study that values above 3% of nanoclay reduce the degree of performance (PG). In their research, Farias *et al.* [19] proved that the addition of nanoclay did not increase PG.

Another parameter obtained together with the degree of performance of asphalt binders is the phase angle. Fig.2 shows the phase angle results obtained for the samples analyzed at the test temperatures of 58 and 64 °C.

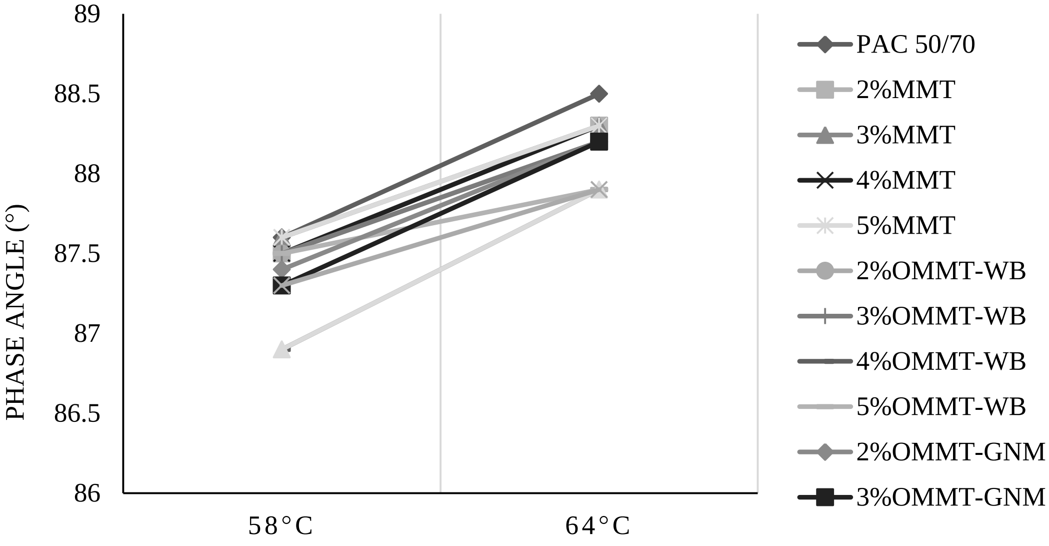

Fig.2 Phase angle for temperatures of 58 and 64 °C

Analyzing Fig.2, the phase angle values obtained for the modified samples did not show significant variation compared to the reference sample (PAC 50/70). Thus, the result corroborates the results presented so far, where the additions of modifying agents did not compromise the asphalt binder, as they are non-reactive compounds to the asphalt binder. However, it is still possible to notice that the samples modified with 4% OMMT-WB and 4% OMMT-GNM had the lowest phase angle values, which would indicate a slight gain in elasticity compared to the reference binder. According to Ayrey [35], this behavior occurs because, at high temperatures, the viscosity of the binder is so low that it allows the elastic network of the polymer to influence the rheological properties of the binder.

The multiple stress creeps and recovery test (MSCR) allowed the evaluation of the percentage of recovery (%R - where elasticity data is provided) of the non-recoverable compilation (Jnr - which presents data on the susceptibility to deformation accumulation permanent, smaller values of Jnr indicate the resistance of the binder to this effect) and the percentage difference between the non-recoverable compilations (Jnr, diff - which provides data on the sensitivity to the increase in the stress level). Table 5 presents the data from the MSCR assay.

The modified samples showed again in elastic properties for a load of 0.1 kPa; even so, this gain cannot be considered relevant considering the magnitude. This is proven by the absence of gain in the load of 3.2 kPa, where the tested samples showed similar results. Finally, it is worth noting a possible sensitivity with the loading variation, where the modified binders showed more significant elastic property losses than the reference samples.

D'Angelo *et al.* [36] comment in their work that Jnr measurements are used to evaluate the properties of binders modified at high temperatures, correlated to the permanent deformation resistance of the asphalt binder. High Jnr values mean the binder's high susceptibility to permanent deformation; on the other hand, the lower the Jnr value, the more excellent the resistance of the modified binder to permanent deformation. Another critical parameter of the MSCR test is the differential Jnr (Jnr, diff), which measures the difference between the Jnr at 0.1 kPa and 3.2 kPa, expressed as a percentage. According to Sobreiro [37], the difference between Jnr under a tension of 0.1 kPa and 3.2 kPa must be less than 75% to attest that the property of the ligand is not overly sensitive to changes in loading. In this way, all the ligands were researched to meet the established criteria.

Table 5. Parameters obtained in the fluency and recovery test

Samples	**Recovery percentage (%)**		**Non-recoverable compilation Jnr (kPa^{-1})**		**Jnr, diff (%)**
	0.1 kPa	3.2 kPa	0.1 kPa	3.2 kPa	
PAC 50/70	0.2	0.1	4.0	4.1	3.7
2% MMT	0.5	0.2	3.6	3.8	4.1
3% MMT	0.5	0.1	3.7	3.8	2.3
4% MMT	0.8	0.2	3.5	3.7	4.3
5% MMT	0.7	0.4	3.0	3.2	4.7
2% MMT-WB	1.9	0.2	3.6	3.7	5.4
3% MMT-WB	0.8	0.1	3.6	3.7	6.7
4% MMT-WB	0.2	0.2	3.7	3.9	4.2
5% MMT-WB	0.8	0.0	4.9	5.5	12.2
2% MMT-GNM	0.5	0.1	4.3	4.5	3.9
3% MMT-GNM	0.2	0.0	4.3	4.5	3.9
4% MMT-GNM	0.7	0.1	3.8	3.9	5.4
5% MMT-GNM	0.6	0.0	4.6	4.9	7.0

According to AASHTO M320:2021, the relation between the values obtained for Jnr at 3.2 kPa and the traffic class in which the linker is found can be made. Table 6 presents this classification.

Table 6. Traffic level capability based on Jnr values

Property	**Jnr (kPa^{-1})**	**Type of traffic**	**Number of passes on a standard axis**
Jnr at 3.2 kPa at the 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 M320:2021

All evaluated ligands are classified to support standard traffic (S), except for the modified samples with 5% OMMT-WB, 2% OMMT-GNM, 3% OMMT-GNM, and 5% OMMT-GNM, which presented values above 4. In addition, the pure linker also presented a value above 4, but as it is very close to the limit, it may be classified as regular traffic (S).

Another factor analyzed in the MSCR test is elastic recovery. According to AASHTO M320:2021, for binders with high Jnr, binders with a high non-recoverable range, there is no specified minimum elastic recovery. The MSCR recovery percentage (%) can detect and quantify the effect of the additive on the binder. They are increasing the percentage values of this parameter, which results in the improvement of a linker modification to maintain elastic characteristics at high traffic levels.

Analyzing the results presented in Table 6, it is observed that all samples had an average Recovery below 10% (except 5% OMMT-WB), proving the analyzes presented so far, in which the additions of modifiers do not seriously compromise the properties of the asphalt binder. It is also possible to observe that the PAC 50/70 is outside the traffic specifications of AASHTO M320:2021. While the additions of MMT and WB provide the adjustment of non-recoverable compilation to traffic limits. Only samples modified with 2 and 4% OMMT-GNM, 3% MMT, and 3%MMT-WB followed the trend shown by the reference binder.

4. Conclusions

From the results obtained, the following conclusions were drawn:

- The incorporation of organophilic montmorillonite showed increased stiffness before and after short-term aging. In addition, all samples showed lower penetration values and higher values of retained penetration, indicating more excellent resistance to aging and being less susceptible to oxidation.
- The use of the organophilic montmorillonite Genamin showed the smallest increase in the softening point, indicating better aging when compared to the other modified samples, retarding the effect of oxidation and volatilization produced by aging in the short term. The addition of the organophilic montmorillonite praepagen WB showed lower thermal susceptibility.
- The montmorillonite showed a gain in viscosity to the binder. Organophilic montmorillonite had higher viscosities than pure montmorillonite. Mainly values above 4%, indicating saturation of the additive, which may present a mischaracterization of its properties.
- Additives did not show variation in the degree of performance (PG). They did not suffer from oxidation at high temperatures but did not show any benefit in this regard. The 4% content of organophilic montmorillonite (WB and GNM) showed lower phase angles, indicating a slight gain in elasticity.
- WB organophilic montmorillonite presented Jnr values close to the binder with pure montmorillonite and lower than PAC 50/70, being less susceptible to permanent deformation.

In general, the incorporation of montmorillonite to the asphalt binder showed a stiffness gain that improved thermal susceptibility and gain in resistance to permanent deformation. The addition of the organophilic montmorillonite praepagen WB was more effective than the organophilic montmorillonite Genamin, showing better results than those found with pure montmorillonite and superior to the reference binder.

Therefore, these changes are desirable when a stiffer binder can be applied in heavier services and at higher usage temperatures; however, to work with this ligand, energy expenditure also increases. On the other hand, the addition of the modifiers MMT-WB and MMT did not show a significant increase in the mixing and compaction temperature, avoiding that the energy costs for heating and compacting the asphalt mass were also high.

References

[1] Dehouche, N., Kaci, M., Mouillet, V., *The effects of mixing rate on morphology and physical properties of bitumen/organo-modified montmorillonite nanocomposites*. Construction and Building Materials, 2016. **114**: p. 76-86. https://doi.org/10.1016/j.conbuildmat.2016.03.151
[2] Golchin, B., Hamzah, M. O., Omranian, S.R., Hasan, M.R.M., *Effects of a surfactant-wax based warm additive on high temperature rheological properties of asphalt binders*. Construction and Building Materials, 2018. **183**: p. 395-407. https://doi.org/10.1016/j.conbuildmat.2018.06.099
[3] Alamdary, Y.A., Singh, S., Baaj, H., *Laboratory simulation of the impact of solar radiation and moisture on long-term age conditioning of asphalt mixes*. Road Materials and Pavement Design, 2019. **20**: p. 521-532. https://doi.org/10.1080/14680629.2019.1587496
[4] Wang, W., Wang, L., Xiong, H., Luo, R., *A review and perspective for research on moisture damage in asphalt pavement induced by dynamic pore water pressure*. Construction and Building Materials, 2019. **204**: p. 631-642. https://doi.org/10.1016/j.conbuildmat.2019.01.167
[5] Ziari, H., Amini, A., Moniri, A., Habibpour, M., *Using the GMDH and ANFIS methods for predicting the crack resistance of fibre reinforced high RAP asphalt mixtures*. Road Materials and Pavement Design, 2019. https://doi.org/10.1080/14680629.2020.1748693

[6] Behnood, A., Gharehveran, M.M., *Morphology, rheology, and physical properties of polymer-modified asphalt binders*. European Polymer Journal, 2019. **112**: p. 766-791. https://doi.org/10.1016/j.eurpolymj.2018.10.049
[7] Du, Z., Jiang, C., Yuan, J., Xiao, F., Wang, J., *Low temperature performance characteristics of polyethylene modified asphalts – A review*. Construction and Building Materials, 2020. **264**. https://doi.org/10.1016/j.conbuildmat.2020.120704
[8] Zheng, X., Easa, S.M., Yang, Z., Ji, T., Jiang, Z., *Life-cycle sustainability assessment of pavement maintenance alternatives: Methodology and case study*. Journal of Cleaner Production, 2019. **213**. https://doi.org/10.1016/j.jclepro.2018.12.227
[9] Heidari, M.R., Heravi, G., Esmaeeli, A.N., *Integrating life-cycle assessment and life-cycle cost analysis to select sustainable pavement: a probabilistic model using managerial flexibilities*. Journal of Cleaner Production, 2020. **254**. https://doi.org/10.1016/j.jclepro.2020.120046
[10] Ezzat, H., El-Badawy, S., Gabr, A., Zaki, E. I., Breakah, T., *Evaluation of Asphalt Binders Modified with Nanoclay and Nanosilica*. Procedia Engineering, 2016. **143**: p. 1260-1267. https://doi.org/10.1016/j.proeng.2016.06.119
[11] Abansansari, H. F., Modarres, A., *Investigating effects of using nanomaterial on moisture susceptibility of hot-mix asphalt using mechanical and thermodynamic methods*. Construction and Building Materials, 2017. **131**: p. 667-675. https://doi.org/10.1016/j.conbuildmat.2016.11.052
[12] Razavi, S., Kavussi, A., *The role of nanomaterials in reducing moisture damage of asphalt mixes*. Construction and Building Materials, 2020. **239**. https://doi.org/10.1016/j.conbuildmat.2019.117827.
[13] Mortezaei, M., Shabani, S., Mohammadian-Gerzaz, S., *Assessing the effects of premixing on the rheological properties for three-phase asphalt binder nano-composite including clay and SBS*. Construction and Building Materials, 2020. **231**. https://doi.org/10.1016/j.conbuildmat.2019.117151
[14] Li, R., Xiao, F., Amirkhanian, S., You, Z., Huang, J., *Developments of nano materials and technologies on asphalt materials – A review*. Construction and Building Materials, 2017. **143**: p. 633-648. https://doi.org/10.1016/j.conbuildmat.2017.03.158
[15] Hussain, C.M., *Polymer nano-composites-An intro*. New Polymer Nanocomposites for Environmental Remediation, 2018. p. 21-25. https://doi.org/10.1016/B978-0-12-811033-1.09997-2
[16] Ashish, P.K., Singh, D., Bohm, S., *Investigation on influence of nanoclay addition on rheological performance of asphalt binder*. Road Materials and Pavement Design, 2017. **18**: p. 1007-1026. https://doi.org/10.1080/14680629.2016.1201522
[17] Zhu, C., Zhang, H., Shi, C., Li, S., *Effect of nano-zinc oxide and organic expanded vermiculite on rheological properties of different bitumens before and after aging*. Construction and Building Materials, 2017. **146**: p. 30-37. http://dx.doi.org/10.1016/j.conbuildmat.2017.04.062
[18] Wang, J., Zhang, H., Zhu, C., *Effect of multiscale nano-composites on performance of asphalt binder and mixture*. Construction and Building Materials, 2020. **243**. https://doi.org/10.1016/j.conbuildmat.2020.118307
[19] Farias, L.G.A. T., Leitinho, J.L., Amoni, B.C., Bastos, J.B.S., Soares, J.B., Soares, S.A., Sant'Ana, H.B., *Effects of nanoclay and nanocomposites on bitumen rheological properties*. Construction and Building Materials, 2016. **125**: p. 873-883. http://dx.doi.org/10.1016/j.conbuildmat.2016.08.127
[20] Vargas, M.A., Moreno, L., Montiel, R., Manero, O., Vázquez, H., *Effects of montmorillonite (Mt) and two different organo-Mt additives on the performance of asphalt*. Applied Clay Science, 2017. **139**: p. 20-27. http://dx.doi.org/10.1016/j.clay.2017.01.009
[21] Amini, A., Ziari, H., Saadatjoo, S.A., Hashemifar, N.S., Goli, A., *Rutting resistance, fatigue properties and temperature susceptibility of nano clay modified asphalt rubber binder*. Construction and Building Materials, 2021. **267**. https://doi.org/10.1016/j.conbuildmat.2020.120946

[22] Jahromi, S.G., Khodaii, A., *Effects of nanoclay on rheological properties of bitumen binder*. Construction and Building Materials, 2009. **23**: p. 2894–2904. https://doi.org/10.1016/j.conbuildmat.2009.02.027

[23] Shafabkhsh, G.H., Ani, O.J., *Experimental investigation of effect of Nano TiO2/SiO2 modified bitumen on the rutting and fatigue performance of asphalt mixtures containing steel slag aggregates*. Construction and Buildings Materials, 2015. **98**: p. 692-702. https://doi.org/10.1016/j.conbuildmat.2015.08.083

[24] Ali, J., Mohd, R.M.H., Hui, Y., Zhanping, Y., Meor, O.H., *Characterization of the rate of change of rheological properties of nano-modified asphalt*. Construction and Building Materials, 2015. **98**: p. 437-446. https://doi.org/10.1016/j.conbuildmat.2015.08.069

[25] Sun, Z., Yi, J., Huang, Y., Feng, D., Guo, C., *Properties of asphalt binder modified by bio-oil derived from waste cooking oil*. Construction and Building Materials, 2016. **102**: p. 496-504. https://doi.org/10.1016/j.conbuildmat.2015.10.173

[26] Melo Neto, O. M., Ferreiro, A. A., Freire, T. S., Silva, G. C. B., Lucena, L. C. F. L., Sousa Neto, V. F., *Rheological Analysis of Asphalt Binders Modified with Hydrated Lime and Titanium Dioxide Nanoparticles*. International Journal for Innovation Education and Research, 2020. **8**: p. 579-598. https://doi.org/10.31686/ijier.vol8.iss11.2787

[27] Marinho Filho, P.G.T., *Rheological evaluation of asphalt binders modified with titanium dioxide nanoparticles*. Masters Dissertation. Department of Civil Engineering. Federal University of Campina Grande, 2017. (In Portuguese). http://dspace.sti.ufcg.edu.br:8080/jspui/handle/riufcg/374

[28] Melo, J.V.S., *Development and study of the rheological behavior and mechanical performance of asphalt concrete modified with nanocomposites*. Doctoral Thesis. Department of Civil Engineering. Federal University of Santa Catarina, 2014. (In Portuguese). https://repositorio.ufsc.br/xmlui/handle/123456789/128794

[29] Tomé, L.G.A., *Effect of adding nanoclays and nanocomposites clay/sbs on the performance of asphalt binders*. Doctoral Thesis. Department of Chemical Engineering. Federal University of Ceará, 2014. (In Portuguese). http://www.repositorio.ufc.br/handle/riufc/10833

[30] Ehinola, O.A., Falode, O.A., Jonathan, G., *Softening point and Penetration Index of bitumen from parts of Southwestern Nigeria*. Nafta, 2012. **63**: p. 319-323.

[31] Bernucci, L.B., Motta, L.M.G., Ceratti, J.A.P., Soares, J.B., *Asphalt Paving: Basic Training for Engineers* 2010, Rio de Janeiro: ABEDA.

[32] Gama, D. A., *Effect of Addition of Reactive, Non-Reactive Polymers and Polyphosphoric Acid and Their Combinations on the Properties of Asphalt Binders*. Doctoral Thesis. Department of Materials Engineering. Federal University of Campina Grande, 2016. (In Portuguese). http://dspace.sti.ufcg.edu.br:8080/jspui/handle/riufcg/15030

[33] Mendonça, A.M.G.D., Melo Neto, O.M., Rodrigues, J.K.G., Silvani, C., Lima, R.K.B., *Physicochemical and rheological effects of the incorporation of micronized polyethylene terephthalate in asphalt binder*. Petroleum Science and Technology, 2022. **40**. https://doi.org/10.1080/10916466.2021.2007124

[34] Asphalt Institute, *Performance Graded Asphalt Binder Specification and Testing*. Superpave Series No. 1 (SP-1), 2010.

[35] Ayrey, G.D., *Rheological properties of styrene butadiene styrene polymer modified road bitumens*. Fuel, 2003. **82**: p. 1709-1719. https://doi.org/10.1016/S0016-2361(03)00146-7

[36] D'Angelo, J., Kluttz, R., Dongre, R. N., Stephens, K., Zanzotto, L., *Revision of the Superpave High Temperature Binder Specification: The Multiple Stress Creep Recovery Test (With Discussion)*. Journal of the Association of Asphalt Paving Technologists, 2007. **76**: p. 123-162.

[37] Sobreiro, F.P., *Effect of the addition of phosphoric acids on the rheological behavior of pure asphalt binders and modified with SBS copolymer*. Doctoral Thesis. Department of Civil Engineering. University of São Paulo, 2014. (In Portuguese). http://www.teses.usp.br/teses/disponiveis/18/18143/tde-28052014-100359/

Conflict of Interests

No potential competing interest was reported by the authors.

Author's Contribution

Loredanna Melyssa Costa de Souza. ORCID: https://orcid.org/0000-0003-0907-3444
Elaboration of the conceptualization, methodology, supervision, validation, draft, editing, and review of the manuscript.

Ana Maria Gonçalves Duarte Mendonça. ORCID: https://orcid.org/0000-0002-4595-2959
Elaboration of the conceptualization, methodology, supervision, validation, draft, editing, and review of the manuscript.

Osires de Medeiros Melo Neto. ORCID: https://orcid.org/0000-0002-2535-0969
Conceptualization, methodology, supervision, validation, draft, editing, and review of the manuscript.

John Kennedy Guedes Rodrigues. ORCID: https://orcid.org/0000-0003-0340-5567
Elaboration of the conceptualization, methodology, supervision, validation, draft, editing, and review of the manuscript.

Robson Kel Batista de Lima. ORCID: https://orcid.org/0000-0001-6917-9895
Editing and review of the manuscript.