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Aging Resistance Evaluation of an Asphalt Mixture Modified with Zinc Oxide

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Abstract: The phenomenon of the oxidation and aging of asphalt binders affects the strength and durability of asphalt mixtures in pavements. Several studies are trying to improve the resistance to this phenomenon by modifying the properties of the binders with nano-particles. One material that shows promise in this field is zinc oxide (ZnO), especially in improving ultraviolet (UV) aging resistance. Few studies have evaluated the effect of these nano-particles on the thermo-oxidative resistance of asphalt binders, and, on hot-mix asphalt (HMA), studies are even more scarce and limited. Therefore, in the present study, the resistance to thermo-oxidative aging of an HMA manufactured with an asphalt binder modified with ZnO was evaluated. An asphalt cement (AC 60–70) was initially modified with 0, 1, 3, 5, 7.5, and 10% ZnO (percentage by weight of asphalt binder; ZnO/AC in wt%), and then exposed to aging in Rolling Thin-Film Oven tests (RTFOT) and a Pressure Aging Vessel (PAV). Penetration, viscosity, and softening point tests were performed on these binders, and aging indices were calculated and evaluated. Samples of HMAs were then manufactured using these binders and designed by the Marshall method, determining the optimum asphalt binder content (OAC) and the optimum ZnO/AC ratio. Control (unmodified) and modified HMA were subjected to short-term oven aging (STOA) and long-term oven aging (LTOA) procedures. Marshall, Indirect Tensile Strength (ITS), and resilient modulus (RM) tests were performed on these mixtures. LTOA/STOA results of the parameters measured in these tests were used as aging indices. In this study, ZnO was shown to increase the thermo-oxidative aging resistance of the asphalt binder and HMA. It also contributed to an increase in the resistance under monotonic loading in the Marshall and ITS tests, and under repeated loading in RM test. Likewise, it contributed to a slightly increasing resistance to moisture damage. The best performance is achieved using ZnO/AC = 5 wt%.

Keywords: aging; hot-mix asphalt; modified asphalt; Zinc oxide; ZnO

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1. Introduction

When an asphalt binder oxidizes and ages, it changes its physicochemical properties [1–3]. These changes directly affect the mechanical properties and durability of asphalt pavements. During oxidation, the asphalt binder increases its stiffness, hardness, and brittleness, and loses cohesion and adhesion with aggregates, increasing the probability of different pavement distress occurrences such as moisture damage, fatigue cracking, pothole, stripping, raveling, surface weathering or erosion, and top-down cracking, among others [4–9]. To decrease the effects of aging in asphalt binders, some researchers recommend modifying them with polymers [10], resins [11], and additives used in warm-mix asphalts—WMA [12], among others. Researchers also recommend the use of rejuvenators [3] and properly balancing the binder–aggregate composition in the design of asphalt mixtures [13]. Several techniques are used to simulate the short-term thermo-oxidative aging of asphalt binders. The most commonly used technique consists of combining heat

(163 °C) and air (4000 mL/min) on a thin asphalt film (approximately 3.2 mm) for 85 min in a Rolling Thin-Film Oven (RTFO), following the guidelines established by ASTM D 2872 or ASHTO T 240. In the case of asphalt mixtures, the most commonly used method is short-term oven aging (STOA), which consists of subjecting the mixture in its loose state to a temperature of 135 °C (using a conventional oven) for two hours, and then compacting it (AASHTO R 30). The simulation of long-term aging of asphalt binders is usually performed using Pressure Aging Vessel (PAV) equipment. Samples previously aged in RTFO are introduced into the PAV to be subjected to 90, 100, or 110 °C (cold, moderate, or hot climate, respectively) and 2.07 MPa for 20 h (AASHTO R 28). On asphalt mixtures, the most commonly used method to simulate long-term oven aging is long-term oven aging (LTOA). In this method, the STOA-aged mixture is subjected to a conventional oven at a temperature of 85 °C for 5 days (AASHTO R 30). In theory, this procedure simulates the aging that the mixture undergoes between 7 to 10 years of pavement service life [1,14].

Likewise, a material that has been showing a high chance of success in improving aging resistance is zinc oxide—ZnO [15–19]. ZnO is a colorless material with low toxicity [20], showing a high compatibility with asphalt binders [21–23], high conductivity, heat capacity, and chemical–thermal stability [24]. It also exhibits a low ultraviolet—UV optical absorption and expansion coefficient [25]. Its nanometer size and piezoelectric properties promote its study as a modifier of asphalt binders that help improve UV aging resistance [26–30]. Ref. [31] modified two asphalt cement—AC (AC 73 and AC 92 dmm) with nano-ZnO (2 wt% to binder mass) and evaluated the morphology and UV aging resistance of both binders. According to them, the aging resistance of ACs improved and the influence of ZnO depends on the AC type. Ref. [32] also modified an AC (3 wt% nano-ZnO), but the nano-particle surface was modified with 3- aminopropyltriethoxysilane, γ—methacryloyloxypropyltrimethoxysilane and γ-(2,3- epoxypropoxy) propyltrimethoxysilane. The UV aging resistance improves with nano-ZnO but changes depending on the surface modifier type. A similar study was reported by [26] but modified with 2 wt% and using c-(2,3-epoxypropoxy) propyltrimethoxysilane. The UV aging resistance is improved, and it is higher when ZnO is surface-modified with c-(2,3-epoxypropoxy) propyltrimethoxoxysilane. [33] reported a study with similar conclusions (AC shows a better UV aging resistance), but comparing the results with two other nanoparticles (nano-TiO_2 and nano-SiO_2). Another similar study reporting an increased UV aging resistance is stated by [34], modifying an AC with ZnO and organically expanded vermiculite—OEVMT (3 wt%). [35] improved an AC (1 wt% of OEVMT) and 1, 2, 3, and 4 wt% (ZnO-modified with two surface modifiers). The optimum content of both materials was 3% ZnO + 1% OEVMT. Researchers found that ZnO negatively influences the physical properties of AC when it exceeds 4 wt%. Similar studies reporting increased UV resistance employing ZnO can be found in Zhu et al. [36,37]. [38] was modified with nano-ZnO (1, 2, 3, 4, and 5 wt%). ZnO improved its rheological properties and stiffness of the AC, and its UV aging resistance. The optimum ZnO content was reported to be 3 wt%. [39] reported similar conclusions and an equal optimum percentage (3 wt%) modifying an AC with rodlike ZnO (0.5, 1, 2, 3, and 4 wt%). [8] modified an AC with vermiculite-EV and ZnO (2, 3, 4, 5, and 6 wt%). ZnO/EV improved binder properties at high temperatures but compromised them at low temperatures. It also improved the performance of asphalt mixtures when ZnO/EV = 5% was used. [15] modified an AC with nano-TiO2/ZnO = 2, 4, 6, and 8 wt%. Researchers also used basalt fiber—BF (6 wt). All three modifiers increase the rutting, fatigue (intermediate temperature), and aging resistance of the binder. The optimum nano-TiO_2/ZnO content was 4 wt%. [40] evaluated the influence of ZnO nanometer size (10–30 nm, 50–70 nm, 100–200 nm) on the morphology, rheological, physical properties, and aging resistance of an AC (PG 64–22) modified with ZnO concentrations of 1, 3, and 5 wt%. ZnO improved the binder elastic performance and rutting resistance. It also increased the short-term (RTFO) and long-term (PAV) aging resistance of the AC. A content of 3–5 wt% of ZnO with a particle size ranging between 10 to 30 nm was recommended.

The use of nano-ZnO as an asphalt binder modifier is a relatively new technique. Few studies have evaluated the influence of ZnO on the aging resistance of binders, and most have focused on analyzing the performance against UV radiation. As asphalt binder modifiers for hot-mix asphalt (HMA), studies are scarcer and more limited [19]. From the literature consulted, only one study evaluated the performance of an asphalt mixture against the effects of thermo-oxidative aging [8], but, in this study, before modifying the binder, the ZnO was previously synthesized with EV to deagglomerate the nano-particles. In contrast to the studies reported in the reference literature, in the present research, the influence that a ZnO (without modifying its surface) has on the thermo-oxidative resistance of an HMA when used as an AC modifier was evaluated. To this end, the AC was modified with 0, 1, 3, 5, 7.5, and 10% ZnO (percentage by weight of asphalt binder; ZnO/AC in wt%), and exposed to aging procedures in RTFO Tests (RTFOT) and PAV. Penetration (ASTM D5), viscosity (ASTM D4402), and softening point (ASTM D36) tests were performed on the residues of these aged binders, and aging indices were calculated and evaluated. HMAs manufactured with these binders were designed by the Marshall method (the optimum asphalt binder content—OAC and the optimum ZnO/AC ratio were determined). Control (unmodified) and modified HMA were subjected to STOA and LTOA thermo-oxidative aging procedures. Marshall (AASHTO T 245), Indirect Tensile Strength (AASHTO T 283), and resilient modulus—RM tests (UNE-EN 12697-26) were performed on these mixtures. The LTOA/STOA ratio of the parameters measured in these tests was used as an indicator of resistance to thermo-oxidative aging.

2. Materials and Methods

2.1. Materials

An AC 60–70 (penetration range in dmm, according to ASTM D5 procedure) was used as an asphalt binder. This AC complies with the quality requirements of Colombian INVIAS standard [41] (see Table 1). To manufacture the HMA mix, an aggregate was used that also met the quality requirements demanded by INVIAS [41] (see Table 2).

Table 1. AC 60–70 properties.

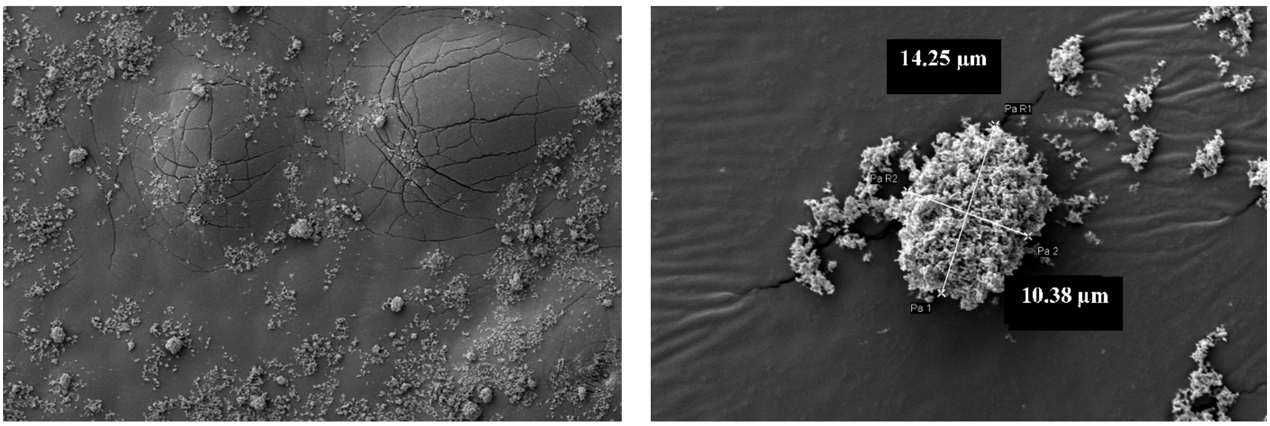
Test	Unit	Method	Result	Recommended
Neat asphalt binder				
Softening point	°C	ASTM D 36	48.7	48–54
Penetration	dmm	ASTM D 5	61.6	60–70
Penetration index	-	NLT 181	−1.05	−1.2 to +0.6
Specific gravity	-	AASHTO T 228	1.024	-
Viscosity (135 °C)	P	ASTM D 4402	4.72	4 minimum
Ductility	cm	ASTM D113	128	100 minimum
Flash and fire points	°C	ASTM D8254	288	230 minimum
After RTFOT				
Mass loss	%	ASTM D2872	0.22	0.8 maximum
Percent penetration retained	%	ASTM D 5	82.8	50 minimum
Increase in softening point	°C	ASTM D 36	2.3	9 maximum

The ZnO used is commercial and over-the-counter (Figure 1). To date, it is a material whose approximate cost is US$ 7.5/kg. At room temperature (20 °C), the coloration of ZnO is white. Its particles (size less than 0.075 mm) were visualized (between 500 and 40,000 magnification) in a scanning electron microscope—SEM (JEOL JSM-6700F) with an accelerating voltage of 4 to 20 kV and a working distance of approximately 4 to 9 mm (Figure 2). ZnO particles and their elemental chemical composition were measured. Based on the observations, ZnO is agglomerated in sizes below 20 µm (Figure 2a–d), and each nano-particle in the agglomeration is tubular with extremely small dimensions (nanometer scale; approximately 200 to 600 nm; e.g., Figure 2d). To disperse these nano-particles, one could use a dispersing agent or mechanism, or modify the ZnO surface as has been recommended in the reference literature [8,19,33,42,43]. However, in the present study, the effect of ZnO without modification was evaluated. The elemental chemical composition shows a high-purity modifier (ZnO). On average, each particle showed Zn and O contents of 80 and 20%, respectively. These values agree with those provided by the supplier: 99.0% ZnO (80.28% Zn, and low bacterial and trace organic content). On the other hand, the specific gravity of ZnO is 5.6 g/cm^3 and it is an alkaline material (pH higher than 7).

Table 2. Aggregate properties.

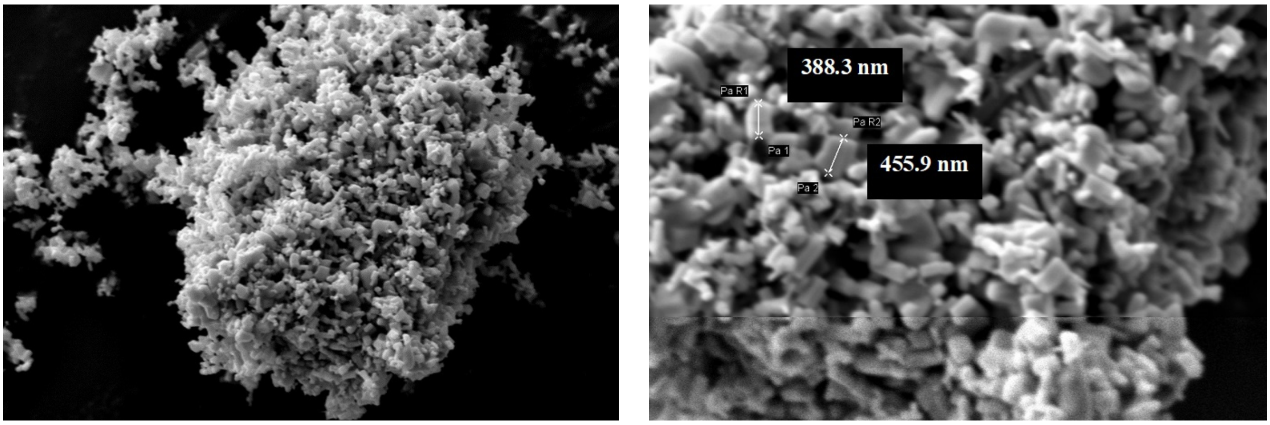
Test	Method	Recommended	Result
Absorption (fine aggregate)	AASHTO T 84, 85	-	1.65%
Absorption (coarse aggregate)		-	1.88%
Specific gravity (fine)		-	2.652
Specific gravity (coarse)		-	2.671
Soundness using magnesium sulphate	AASHTO T 104	18.0% maximum	5.3%
Fractured particles (1 side)	ASTM D5821	85% minimum	92.7%
Abrasion in Los Angeles machine	AASHTO T 96	25% maximum	22.7%
10% of fines (dry resistance)	DNER-ME 096	110 kN minimum	122.5 kN
10% of fines (wet resistance)	DNER-ME 096	82.5 kN minimum	108.9 kN
Micro-Deval	AASHTO T 327	20% maximum	18.6%

Figure 1. Zinc oxide—ZnO.



(**a**) (**b**)

Figure 2. *Cont.*



(**c**) (**d**)

Figure 2. (**a**) ZnO at 500 X.; (**b**) ZnO at 6000 X; (**c**) ZnO at 15,000 X; and (**d**) ZnO at 40,000 X.

2.2. Asphalt Binder Modification and Aging Assessmen

AC was modified using addition percentages of 1, 3, 5, 7.5, and 10% (respect to mass of AC; ZnO/AC = 1, 3, 5, 7.5, and 10 wt%). Mixing was performed in high shear equipment at 155 ± 5 °C and 4000 rpm. These addition percentages, temperature, and mixing speed were chosen based on the literature review [19]. Technical and environmental criteria were also taken into account (not to use very high temperatures to avoid aging of the binder, as well as increased pollutant emissions and production costs; [44]). The mixing time (MT) varied between 30, 60, and 90 min. This time range was chosen, taking into account experiences from previous studies reported on the subject [19]. The modified asphalt binders were exposed to short-term aging in RTFOT (163 °C for 85 min; AASHTO T 240). These samples were also conditioned for long-term aging (AASHTO R 28) in a PAV equipment (the residue obtained from RTFOT was subjected to 2.07 MPa at 100 °C for 20 h). Penetration (ASTM D 5), softening point (ASTM D 36), and viscosity at 135 °C (ASTM D 4402) tests were performed on samples of unaged, RTFOT-aged, and RTFOT + PAV-aged modified asphalt. The results obtained from these tests were used to calculate aging indices (Penetration Decrease Index—*PDI*, Softening Point Increment—*SPI*, and Viscosity Aging Index—*VAI*), calculated according to Equations (1)–(3). *AP* and *UP* are aged and unaged penetration, respectively, in dmm. *ASP* and *USP* are aged and unaged softening points, respectively, at °C. *AV* and *UV* are aged and unaged viscosity at 135 °C, respectively, in cP. Based on these tests and evaluation indices, the MT was chosen and the effect of ZnO on the resistance to thermo-oxidative aging of the binder was evaluated.

$$PDI = \frac{AP}{UP} \tag{1}$$

$$SPI = ASP - USP \tag{2}$$

$$VAI = \frac{AV}{UV} \tag{3}$$

2.3. Asphalt Mixture Design and Choice of ZnO/AC Ratio

Once the AC 60–70 was modified with ZnO (ZnO/AC = 1, 3, 5, 7.5 and 10 wt%) at 150 °C, 4000 rpm, and MT chosen from the previous phase, the performance of the HMA mixtures was evaluated using the Marshall method (AASHTO T 245). A total of six types of mixes were analyzed: the Control HMA with ZnO/AC = 0 wt% and five modified mixes (ZnO/AC = 1, 3, 5, 7.5, and 10 wt%). The aggregate particle size distribution is shown in Table 3. This gradation is for HMA-19 according to INVIAS [41]. The mixes were manufactured using four binder contents (4.5, 5.0, 5.5, and 6.0%). The mixing and compaction temperatures were 155 and 145 °C, respectively (viscosity of 170 ± 20 cP and

280 ± 30 cP, respectively). Three Marshall samples for each mixture type and asphalt content were manufactured. The samples were compacted by applying 75 blows per face. Voids filled with asphalt—*VFA*, air void content—*Va*, flow—*F*, stability—*S*, and *S*/*F* ratio were determined for each sample. *S* and *F* were determined at 60 °C, applying in a Marshall compression machine, a monotonic loading rate of 50.8 mm/minute. With the results obtained from the Marshall test, the OAC and the ZnO/AC ratio were chosen. These parameters were used to manufacture the samples in the subsequent experimental phases. The design criteria for choosing the OAC are those established by INVIAS [41].

Table 3. HMA-19—Particle size distribution.

Sieve, mm	19.0	12.5	9.5	4.75	2.0	0.43	0.18	0.075
Sieve	¾″	½″	3/8″	#4	#10	#40	#80	#200
Passing, %	100	87.5	79.0	57.0	37.0	19.5	12.5	6.0

2.4. Mechanical Strength and Aging Analysis

Indirect Tensile Strength—ITS, Marshall, and resilient modulus—RM tests were performed to evaluate the mechanical strength and measure aging rates of the control (unmodified; ZnO/AC = 0 wt%) and modified (ZnO/AC = 5%, chosen from the previous phase) HMA mixes. These tests were performed on samples subjected to STOA and LTOA aging protocols. Following the recommendations of AASHTO R30, to simulate the STOA condition, the samples were initially heated during 4 h at 135 °C in a loose state in a conventional laboratory oven, and then compacted at 75 blows (per face). LTOA condition was simulated after the STOA process; the samples were kept for five days in an oven at 85 °C. The LTOA/STOA ratios of each of the strength parameters measured for each test were measured as an index of aging.

The Marshall test was performed on three samples per type of mixture (ZnO/AC = 0 wt% subjected to STOA and LTOA, and ZnO/AC = 5 wt% subjected to STOA and LTOA) following the process described in the previous experimental phase (Section 2.3) and the guidelines of AASHTO T 245. The strength parameter evaluated was the *S*/*F* ratio (also known as Marshall Quotient), which is an indirect indicator of stiffness under monotonic loading. ITS tests were performed on three dry samples (*ITSD*) and three conditioned samples (immersed in water for one day in a water bath at 60 °C; *ITSC*) per type of mix, following the guidelines of AASHTO T 283. The *Va* of the mixes in the ITS test varied between 7 ± 0.5%. *ITSD* and *ITSC* were measured at 25 °C applying a loading rate of 50 mm per minute in the Marshall compression machine. The *ITSC*/*ITSD* ratio was used to calculate the Tensile Strength Ratio (*TSR*) to evaluate the resistance to moisture damage. The RM was measured per type of mixture at 10, 20, and 30 °C, and frequencies of 2.5, 5, and 10 Hz, using a Nottingham Asphalt Tester (NAT), following the guidelines of UNE-EN 12697-26.

2.5. ANOVA—Analysis of Variance

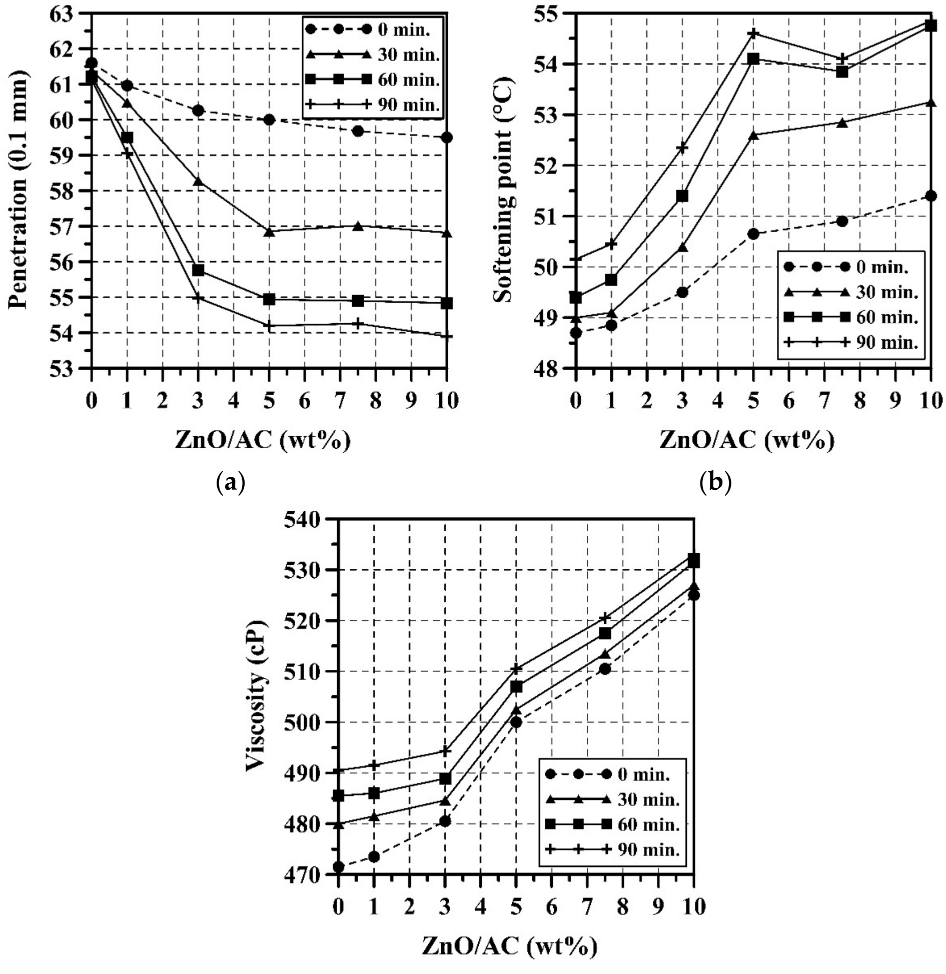
To evaluate whether the changes observed in the measured properties due to the use of ZnO were statistically significant, an ANOVA—analysis of variance (F-test) with 95% confidence was performed. In the F-test, an $F > F_{0.05}$ means that the measured change in the evaluated property is statistically significant.

3. Results

3.1. Modified Asphalt Properties and Aging Assessment

The penetration, softening point, and viscosity test results performed on unmodified (ZnO/AC = 0 wt%) and modified (ZnO/AC = 1, 3, 5, 7.5, and 10 wt%) AC 60–70 are shown in Figure 3a–c, respectively. This figure also shows the effect of MT during the modification process (30, 60, and 90 min). As the MT and ZnO/AC content increases, the binder stiffens (the penetration decreases and the softening point and viscosity increase).

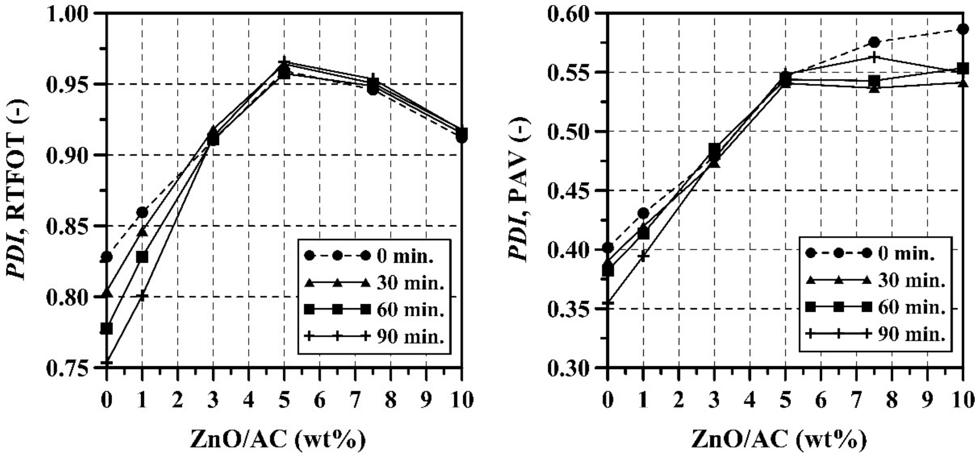
At ZnO/AC = 1 wt%, the changes are not significant. Figure 3a,b shows that the highest rate of decrease in the penetration and increase in the softening point is achieved when ZnO/AC = 5 wt%. From this value onwards, these rates decrease. Viscosity, on the other hand, increases with ZnO/AC content. The above is mainly because ZnO nano-particles increase the internal friction forces in the binder during the test [1]. Additionally, ZnO presents a high specific surface area, facilitating the adsorption of light components on the binder [45]. The gain in binder stiffness due to ZnO is also explained by the high mechanical strength and structural stability of the nano-particles, which have been shown in rheology tests to increase rutting resistance [18,42].



(**a**) (**b**) (**c**)

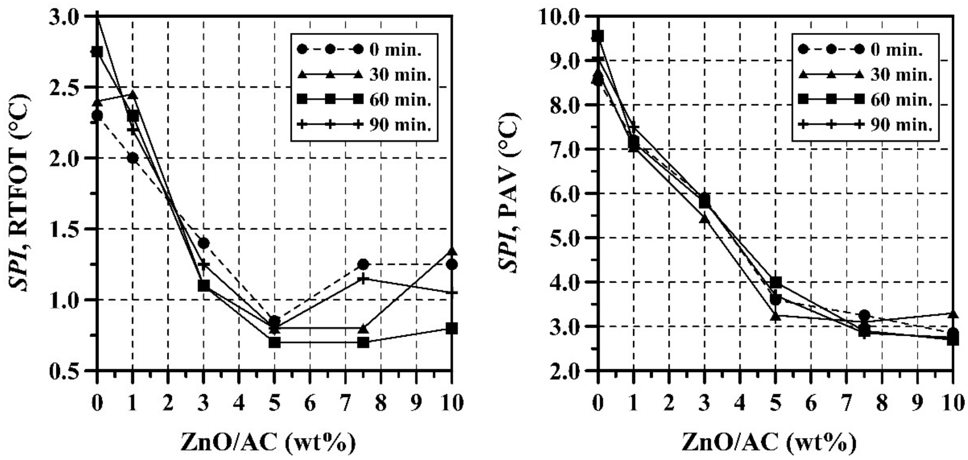
Figure 3. Evolution of (**a**) penetration, (**b**) softening point, and (**c**) viscosity with ZnO/AC content and MT.

As AC 60–70 ages, the penetration decreases, and softening points and viscosity increase. The above has been widely reported in the reference literature (e.g., [46–48]). The asphalt binder is a colloidal dispersion composed of asphaltenes (A) within an oily matrix (maltenes—M) composed of aromatic naphthenes (Ar), saturated agents (S), and resins (R) [1,49]. The oily component of the binder tends to be lost during oxidation, restructuring its molecular composition (the fraction of asphaltenes increases and maltenes decrease, stiffening and causing the brittleness of the binder; [50,51]). Additionally, oxidation increases the molecular weight and large molecular size (LMS), generating increases in viscosity [52–54]. On the short (RTFOT)- and long (PAV)-term aged samples, *PDI*, *SPI*, and *VAI* indices were measured (Figures 4–6, respectively). It is observed that the aging resistance improves when ZnO is used since *PDI* increases and the *SPI* and *VAI* indices decrease. The best performance is observed with ZnO/AC = 5 wt%. Di et al. [16], based on liquid-state nuclear magnetic resonance (NMR) spectroscopy tests, report an increase in the percentage of aromatic carbon in an asphalt binder when ZnO is used as a modifier to explain the increase in thermo-oxidative resistance. According to Zhu et al. [40], performing Fourier-Transform Infrared Spectroscopy (FTIR) tests, nano-ZnO modified binders show lower carbonyl and sulfoxide ratios after the aging of RTFO and PAV relative to the unmodified binder. On the other hand, an increase in MT generates the greater oxidation and aging of the samples due to the longer exposure time to which the binders are subjected to high temperatures [55], which could promote the increase in the asphaltenes fraction and the asphaltenes/resins ratio, as well as the decrease in the aromatics content [56,57]. Taking into account the literature consulted and to avoid excessive oxidation of the binder, an MT = 60 min was chosen. Additionally, it is observed in Figure 3a–c that the modified binders undergo similar values of penetration, softening point, and viscosity when using MT = 60 or 90 min.



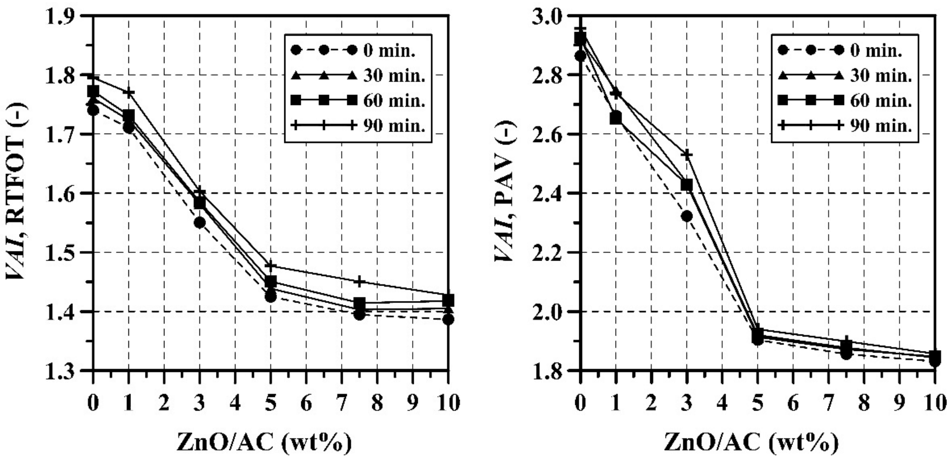
(a) (b)

Figure 4. Evolution of *PDI* with ZnO/AC content and MT. (**a**) RTFOT, and (**b**) PAV.



(a) (b)

Figure 5. Evolution of *SPI* with ZnO/AC content and MT. (**a**) RTFOT, and (**b**) PAV.

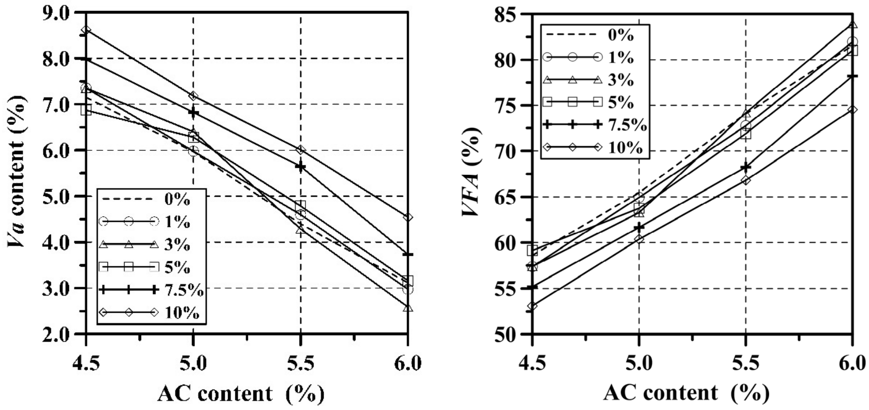


(**a**) (**b**)

Figure 6. Evolution of *VAI* with ZnO/AC content and MT. (**a**) RTFOT, and (**b**) PAV.

3.2. Mixture Design and Choice of ZnO/AC Ratio

The Marshall test results for choosing the OAC and the ZnO/AC ratio are shown in Figure 7. As the ZnO/AC ratio increases, the mixtures tend to be more porous (Figure 7a,b). This is because the ZnO particles increase the viscosity of the binder, making the workability of the mixture and its compaction more difficult. The modified mixture with ZnO/AC = 1 wt% performs similarly in the Marshall test to the Control mix. For the case of the S/F ratio, for example, the ANOVA analysis reports no significant change ($F = 0.87 < F_{0.05} = 7.71$). The changes in strength under monotonic loading (S, S/F) are statistically significant concerning the Control mixture from a ZnO/AC $\geq$ 3%. The maximum S/F ratio is obtained when using ZnO/AC = 5 wt% and an AC content of 5.5% (Figure 7c,d). With this ZnO/AC and AC content, HMA undergoes a 17.7% increase in this parameter concerning the Control mixture, and this increase is statistically significant ($F = 64.2 > F_{0.05} = 7.71$). The nano-oxides tend to form with the binder a structure that increases the yield stress [38]. Additionally, the volumetric design criteria (*Va* between 3 to 5% and *VFA* between 60 to 75%; Figure 7a,b) recommended by the INVIAS [41] standard are met at this ZnO/AC and AC content. A higher ZnO/AC content could be used; however, the changes in the S/F ratio are smaller, and a higher AC (increasing manufacturing costs) is required to meet the volumetric criteria. Therefore, OAC = 5.5% and ZnO/AC = 5 wt% were chosen. Although it is not an objective of this study, an approximate increase of 30% in the cost of m^3 of HMA is estimated (without taking into account the cost of the binder modification process).



(**a**) (**b**)

Figure 7. *Cont.*

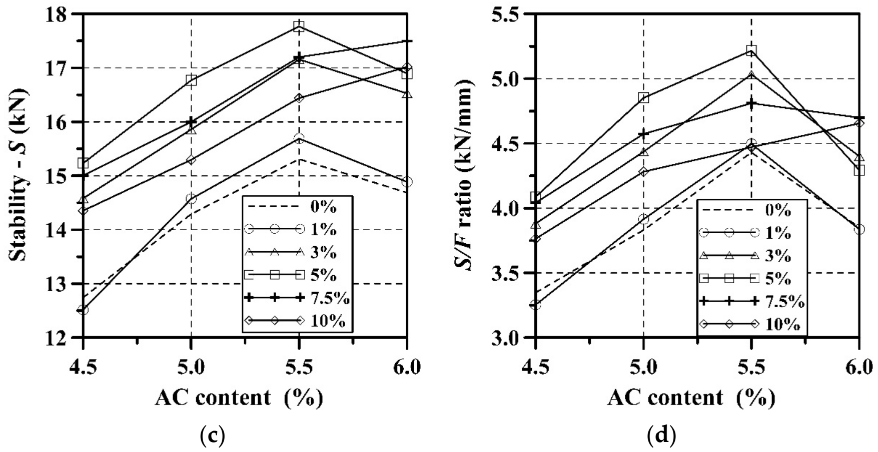


Figure 7. Marshall test results. (**a**) Stability, (**b**) *S*/*F* ratio, (**c**) *Va*, and (**d**) *VFA*.

3.3. Mechanical Strength and Aging Analysis

3.3.1. Marshall Test

The *S*/*F* ratios obtained from the Control sample and the one modified with ZnO/AC = 5 wt% (ZnO) in the STOA and LTOA condition are shown in Figure 8. When the LTOA/STOA ratio is calculated, the value of the Control mixture (LTOA/STOA = 1.19) is higher for the one modified with ZnO (LTOA/STOA = 1.11). In other words, the ZnO mixture tends to stiffen less and is, therefore, more resistant to thermo-oxidative aging. In this test, it is also possible to relate the *S*/*F* values obtained from the unaged—U (Figure 7d) and aged (Figure 8) mixtures. The STOA/U ratio = 1.26 for the Control mixture, while, for the ZnO mixture, the STOA/U parameter = 1.11. This ratio also indicates that ZnO is a material that helps to decrease the oxidation and aging processes in the analyzed mixture. These results are consistent with previously reported *PDI*, *SPI*, and *VAI* values, which show that the ZnO-modified asphalt binder undergo smaller growths in stiffness when exposed to short-term (RTFOT) and long-term (PAV) aging processes.

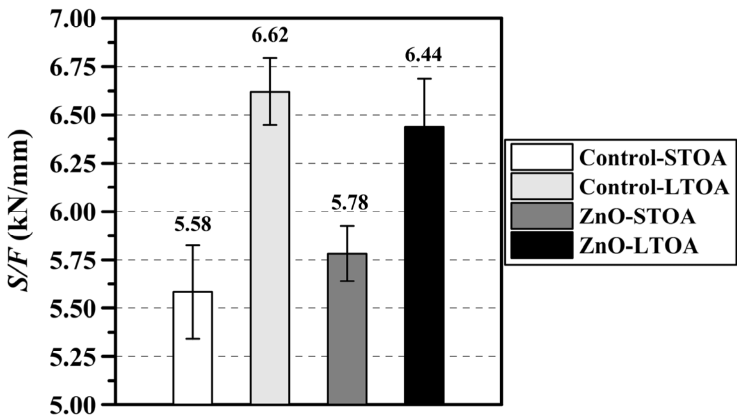


Figure 8. *S*/*F* ratio—Control and modified samples under STOA and LTOA condition.

3.3.2. Indirect Tensile Strength (ITS) Test

The ITS test results are shown in Figure 9. The *ITSD* and *ITSC* parameters of the ZnO blend are higher than the Control mixture, and the changes are statistically significant. In the STOA condition, the *ITSD* of the ZnO mixture is 21.7% higher than the Control mixture ($F = 163.4 > F_{0.05} = 7.71$), and the increase in *ITSC* is 23% ($F = 140.0 > F_{0.05} = 7.71$). In the LTOA condition, the increase in *ITSD* of the ZnO mixture concerning the Control mixture is 8.1% ($F = 10.5 > F_{0.05} = 7.71$), while, in *ITSC*, it is 8.7% ($F = 9.5 > F_{0.05} = 7.71$). On the other hand, in the STOA and LTOA conditions, the Control mixture presents TSR = 86.5 and 82.7%, respectively, while these values are 87.4 and 83.1% in the ZnO mixture. In other words, ZnO contributes to significantly increasing the indirect tensile strength and slightly increasing the resistance to moisture damage. The above is possible because ZnO reduces the acidic component and increases the basic component, increasing the Surface Free Energy (SFE) and improving the binder–aggregate adhesion [58–60]. An increase in binder stiffness by the presence of ZnO (Figure 3) could contribute to increasing *ITSD* and *ITSC* [61–63]. Additionally, ZnO has been shown to increase the peak stress in shear stress–strain curves obtained from linear amplitude sweep (LAS) tests [16], and enhance the bitumen/aggregate adhesion since it generates a network within the structure of the binder, generating a strong connection between the functional groups of the binder and the nano-particles [64]. On the other hand, the *ITSD* LTOA/STOA ratio is 1.29 and 1.15 for the Control and ZnO mixture, respectively. These values change to 1.24 and 1.09, respectively for the case of *ITSC*. In other words, ZnO tends to decrease the stiffness and hardening of the binder during aging processes, which is consistent with the *PDI*, *SPI*, and *VAI* indices calculated on the asphalt binders analyzed (AC 60–70 modified and unmodified).

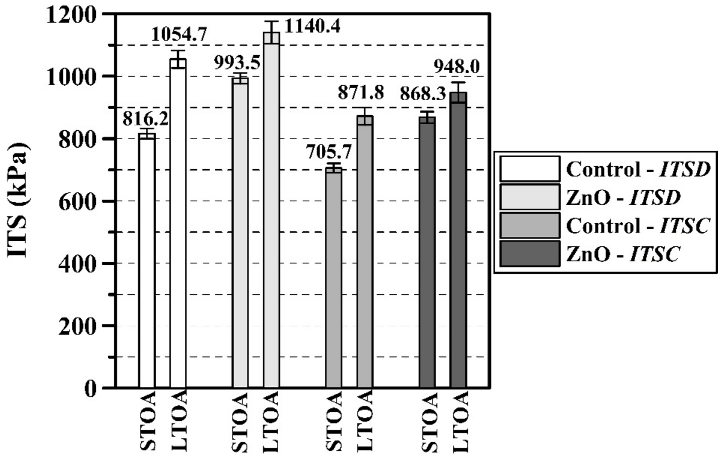


Figure 9. ITS test results.

3.3.3. Resilient Modulus Test

The RM test results are presented in Figure 10. In the STOA condition, ZnO contributed to an increase in the stiffness under the cyclic loading of HMA at temperatures of 20 and 30 °C for any loading frequency (*Fr*), and these increases were statistically significant (Table 4; $F > F_{0.05} = 7.71$). The increase in stiffness is consistent with the decrease in penetration and the increase in viscosity and softening point that AC undergoes when modified with ZnO. Moreover, based on the rheological characterization, the reference literature shows that ZnO helps to increase rutting resistance [16,28,36–38,42,60,65]. The high surface-to-volume ratio of ZnO nano-particles to the asphalt binder can increase the viscosity and adhesion, and improve the functional performance of bitumen, increasing stiffness and decreasing its sensitivity to rutting [64]. At 20 °C, the ZnO mixture in the STOA condition (ZnO-S) underwent an increase in stiffness (between 3.3 and 9.3%) for the Control mixture (Control-S). This increase ranged from 25.2 to 46% at 30 °C. At 10 °C, the ZnO-S mixture decreased stiffness by approximately 2% concerning the Control-S mix, which could be beneficial in reducing cracking in low-temperature climates. In the LTOA condition, the behavior changes because the LTOA/STOA ratio of the RM values is lower in the ZnO-L mixture than in the Control-L mixture (Table 5). When changing from the STOA to LTOA condition, the increase in RM in the Control mixture varies between 12.7 and 24.1% (depending on the test temperature), while this increase in the ZnO mixture is about 5%. In other words, ZnO helps to decrease stiffness during thermo-oxidative aging processes, which is an indicator of increased aging resistance. As in the Marshall test, the lower LTOA/STOA ratio of the ZnO mixture can be explained based on the higher *PDI* values and the decrease in *SPI* and *VAI* undergone by the modified asphalt binder for the unmodified AC 60–70.

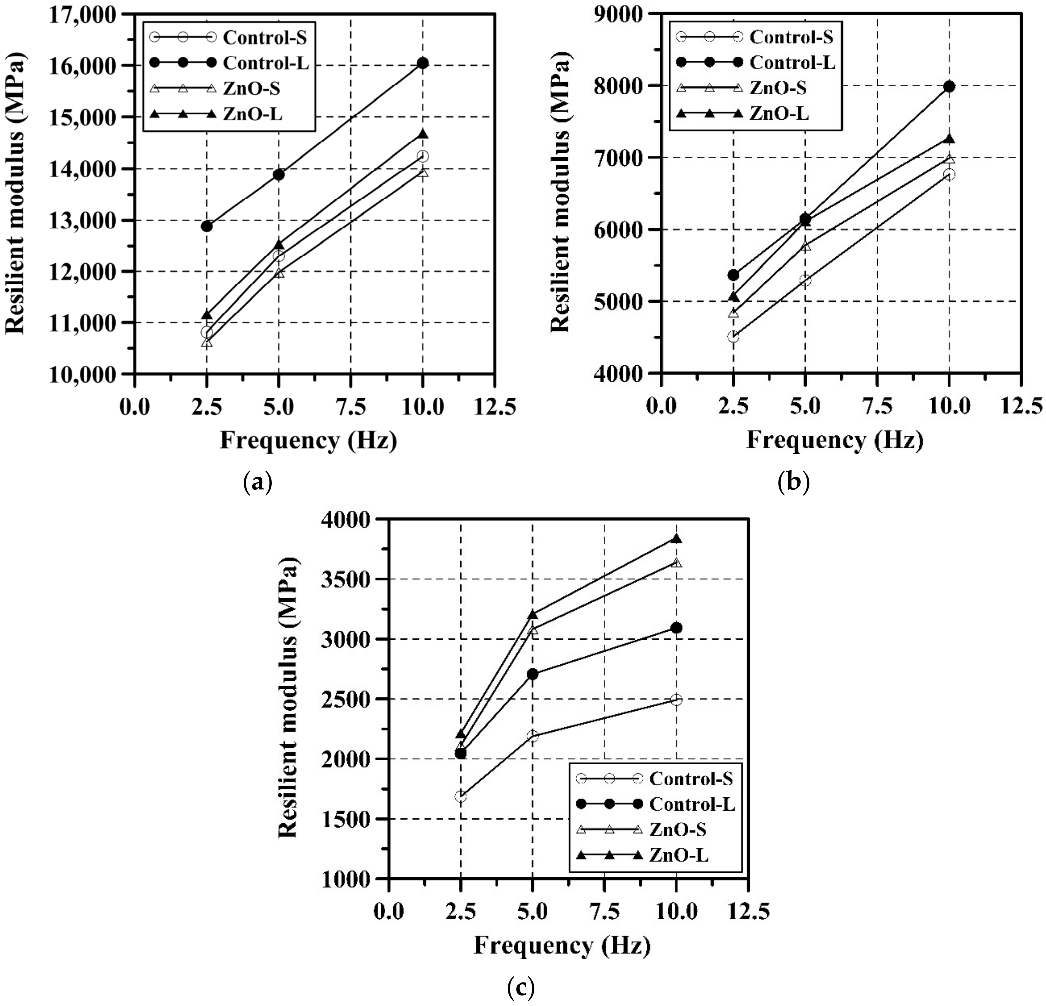


Figure 10. RM test results. (**a**) 10 °C, (**b**) 20 °C, and (**c**) 30 °C.

Table 4. F-test ANOVA for RM tests.

Fr (Hz)	Control-S ZnO-S	Control-L ZnO-L	Control-S ZnO-S	Control-L ZnO-L	Control-S ZnO-S	Control-L ZnO-L
	10 °C		20 °C		30 °C	
	F					
2.5	2.8	906.2	8.3	28.9	9.7	1.37
5.0	11.2	127.7	15.1	0.2	61.0	23.2
10.0	13.2	134.5	12.7	119.0	65.2	28.9

Table 5. LTOA/STOA ratio of RM values.

Fr (Hz)	LTOA/STOA—Control			LTOA/STOA—ZnO		
	10 °C	20 °C	30 °C	10 °C	20 °C	30 °C
2.5	1.191	1.189	1.213	1.050	1.050	1.048
5.0	1.129	1.162	1.237	1.046	1.057	1.041
10.0	1.127	1.180	1.241	1.054	1.040	1.056

4. Conclusions

This study evaluated the influence of ZnO as a modifier of an asphalt binder and its effect on the thermo-oxidative resistance of an HMA mixture. Based on the results obtained, the following is concluded:

- The *PDI*, *SPI*, and *VAI* parameters show that ZnO increased the resistance to thermo-oxidative aging of the asphalt binder. The best performance was achieved with ZnO/AC = 5 wt%. Considering the LTOA/STOA ratio calculated from the *S*/*F*, *ITSD*, *ITSC* and *RM* parameters, ZnO (ZnO/AC = 5 wt%) contributes to increasing the resistance to thermo-oxidative aging of the HMA mixture.
- The stiffness and viscosity of the binder increase with increasing ZnO content. This is mainly when the ZnO/AC ratio $\geq$ 3 wt%. Additionally, the resistance under monotonic loading in the Marshall test (*S*/*F*) and the resilient modulus at 20 °C and 30 °C of the HMA increase when ZnO (ZnO/AC = 5 wt%) is used as a binder modifier. That is, ZnO could help to increase the rutting resistance.
- The *ITSD*, *ITSC*, and *TSR* parameters increase when the HMA uses the ZnO/AC = 5 wt% modified binder. This is an indicator of increased indirect tensile strength and moisture damage resistance.
- ZnO is shown to be a promising nano-material for improving the performance of binders and asphalt mixtures in pavements. Some recommendations for future studies are as follows: (i) evaluate the effect of ZnO on other properties such as fatigue resistance and low service temperatures; (ii) perform direct rutting resistance tests; (iii) use different types of binders, aggregates, and asphalt mixtures; (iv) perform environmental assessment, Life Cycle Cost Analysis (LCCA), and Life Cycle Assessment (LCA); (v) perform storage stability tests on the modified asphalt binder; and (vi) evaluate aging indices obtained from parameters measured at low and intermediate temperatures on asphalt binders (e.g., rheological characterization) and HMAs modified with ZnO.

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