Experimental Investigation of Polymer and Nanomaterial modified Asphalt Binder

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ABSTRACT

Modifying the asphalt binder and mixture becomes one of the best ways to mitigate pavement distress and increase the service life of constructed road networks. This study aimed to evaluate the influence of modified asphalt binders with the best different percentages of polymer and nanoparticles. Typical asphalt binder (penetration, softening point, and viscosity) and frequency sweep tests were used to evaluate the physical and rheological properties of modified asphalt binders with 5% Acrylonitrile Styrene Acrylate (ASA), 5% aluminum oxide nanoparticles (Al_2O_3), and 5% calcium carbonate ($CaCO_3$). The results showed that the physical properties of all modified blends improved compared to those of the base asphalt binder. The improvement in softening point was up to 19%, the penetration reduction was nearly 69%, and the sensitivity to elevated temperatures was reduced by up to 13%. Evaluation of the rheological properties showed that modified asphalt with 5% Al_2O_3 binder had the highest permanent deformation resistance, followed by 5% ASA. The 5% CaCO3 binder showed a small improvement compared to the other samples. The results showed that the 5% Al_2O_3 binder had the highest complex modulus and the lowest phase angle, which means that it has the best viscoelastic properties. Therefore, it can be recognized as the best asphalt binder among the modified binders in this study.

Keywords-modified asphalt binder; acrylate styrene acrylonitrile; polymer; physical and rheological properties; nanoparticles

I. INTRODUCTION

Asphalt pavement is used in motorways and urban streets due to its convenience, ease of maintenance, wear resistance, and fast traffic setting time. Asphalt concrete has become the most common pavement surface worldwide [1]. Classic surface road pavement is commonly a component of asphalt, which is a flexible black adhesive hydrocarbon material, mineral aggregate, and filler materials. These elements are more likely to work together to resist road deformation [2]. Many roads around the world are influenced by challenging environmental conditions, aging issues, and increased load traffic, which results in cracks and ruts [3-4]. Numerous studies have been conducted to investigate the appropriate additive materials to improve pavement performance. In [5], the characteristics of modified asphalt binder with calcium carbonate ($CaCO_3$) and aluminum oxide (Al_2O_3) nanoparticles were investigated at elevated temperatures, showing excellent compatibility and higher storage stability. The stiffness of the modified binders improved with an additional increase in the modifier rate, reaching up to 5% in terms of rheological properties and indicating better resistance to permanent deformation. In [6], polymer/nanocomposite-modified asphalt binders were shown to be significantly improved compared to the base asphalt binder. In [7], the effects of carbon nanofibers on performance-modified asphalt with liquid epoxidized natural rubber were evaluated, showing an increase in stiffness and a reduction in temperature susceptibility. The addition of carbon nanofibers significantly increased the bonding properties between the base and rubberized binders. The optimal content of the modifiers was found to be 0.4% with 6% LENR. Using high percentages (7-8%) of Styrene-Butadiene-Styrene (SBS) polymer to modify the asphalt binder results in superior performance compared to a lower amount of polymer (3%) [7].

In [8], the influence of the nanomaterial-modified asphalt binder and basalt fiber was investigated, showing that the modification of the asphalt binder can mitigate permanent deformation and rutting. In [9], modified asphalt with SBS nanomaterials showed an improvement in compatibility between SBS and asphalt mixtures, using rheological and physical property tests, increasing the storage stability of modified asphalt binders. The mechanical characteristics of modified asphalt binders are mainly affected by the properties of pure bitumen, the modifier, the blending condition, and the interaction of the modifier with bitumen [10]. Asphalt binders are often modified to improve one of the fundamental asphalt attributes, such as stiffness, elasticity, fragility, and strain resistance, but also resistance to cumulative devastation [11]. Polymers are one of the most commonly modified asphalt materials. The addition of polymers to bitumen binders improves both physical and rheological properties, and various studies have shown that it improves the viscoelastic characteristics of the binder by broadening the temperature range resulting in increased resistance to thermal stress and rutting [12-13]. Polymer-modified asphalt mixes can improve the bonding of binder aggregate particles, improving the durability of the pavement. Polymers generally contribute 3.0% to 7.0% of the sample weight [12]. A variety of polymers have been effectively integrated with bitumen concrete engineering, which can be classified into two categories, namely elastomers and thermoplastic elastomers [14-15]. Thermoplastic elastomers have the potential to offer sufficient tension strength when they are subjected to high levels of strain. Researchers have prioritized their investigation over plastomers due to their ability to return to their original shape after stretching. SBS is a common thermoplastic elastomer that is compatible with asphalt [16]. Common types of plastomers that are highlighted to improve the high-temperature capability of asphalt are Ethylene Vinyl Acetate (EVA), Polypropylene (PP), and Polyethylene (PE) [17]. Although blended polymers with asphalt concrete play an important role in improving the physical and rheological properties of asphalt, several studies have observed a significant flaw in the modifying process. The additive polymer must be compatible enough with bitumen concrete to form a homogenous combination and eliminate the separation issue during storage, delivery, and implementation. Furthermore, insufficient aging tolerance is a challenge related to polymer-modified asphalt [18-19].

This study aims to evaluate the effects of modified asphalt binders with different percentages of polymers and nanoparticles, focusing on the performance comparison of the best percentages of modifiers.

II. MATERIALS AND METHODS

A. Materials

The unmodified asphalt binder used had a 60/70 penetration grade as a reference. One binder was modified with polymer, namely, 5% ASA, and the other two binders were modified with nanoparticles, namely 5% Al_2O_3 and 5% $CaCO_3$. The modified asphalt binders were produced in the laboratory using polymers and nanoparticles. The ASA polymers, nano Al_2O_3 and $CaCO_3$ were in powder form. Table I shows the physical properties of the examined asphalt binders.

TABLE I. PHYSICAL PROPERTIES OF BASE AND MODIFIED ASPHALT BINDERS

Material	Properties	Unit	Value
Asphalt 60/70	Specific gravity	-	1.03
	Penetration @ 25°C	0.1 mm	70
	Softening point	°C	47
	Viscosity @ 135°C	(Pa.s)	≤ 3
	Ductility @ 25 C	mm	≤100
	Powder form	-	-
ASA	Size	mm	2
	Powder form	-	
Al_2O_3	Size	nm	13
	Powder form	-	-
$CaCO_3$	Size	nm	40
	Powder form	-	-

B. Sample Preparation

The samples of ASA, Al_2O_3, and $CaCO_3$ were prepared using the melt method. The modifiers were added and blended with the base asphalt binder using a Silverson high shear mixer at a speed of 5000 rpm and at 170 °C for 1.5 hr to produce homogenous mixtures [5, 20-21].

III. RESULTS DISCUSSION

A. Effect of the Modifier on the Penetration of Binders

Figure 1 depicts the penetration values of the different binders. The unmodified binder had the highest penetration value of 70 dmm followed by $CaCO_3$, and Al_2O_3 binders with values of 40 and 25.45 dmm, respectively. In addition, the 5% ASA binder had the lowest penetration value. These results indicate that the binder modified with ASA is stiffer than others, due to the particle uniform distribution of the polymer compared with nanoparticles that face agglomeration due to particle size [5].

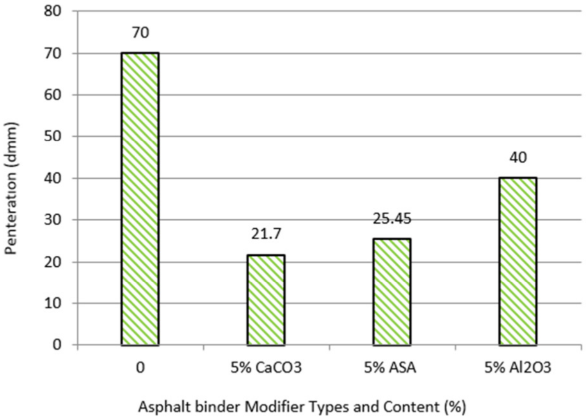

Fig. 1. Penetration test of unmodified and modified binders.

B. Effects of the Modifier on the Softening Point of Binders

The softening point is used to determine the temperature at which a phase change occurs in the binder under standardized conditions. A high softening point indicates low temperature susceptibility and vice versa. Figure 2 shows that the base binder had the lowest softening point temperature at 47°C and the modified binders had relatively higher. The 5% ASA binder had the highest softening point temperature (56 °C), followed by the 5% CaCO3 binder at 54°C, while the 5% Al_2O_3 binder had the lowest (53°C), which was still better than base asphalt. The modified binders generally had better resistance to rutting. The 5% ASA binder had the greatest tendency to resist deformation at intermediate to high temperatures.

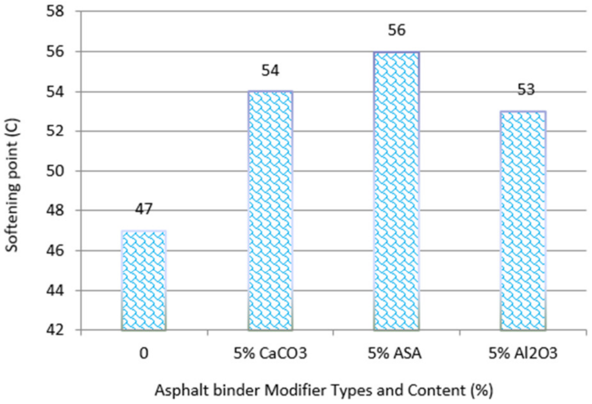

Fig. 2. Softening point of unmodified and modified binders.

C. Viscosity

Viscosity is the binder's resistance to flow during the contraction period. Figure 3 shows a reduction in viscosity with increasing test temperatures, as the mixture slowly moves from the solid to the liquid state. At a predetermined temperature on the viscosity/temperature scale, the viscosity of the modified binders was higher compared to the unmodified binder for most parts of the test, indicating that the modified binders had better performance at high temperatures. This indicates how workable the binder will be. All viscosity values were within the limitations of the Superpave, as they were less than 3 Pa.s.

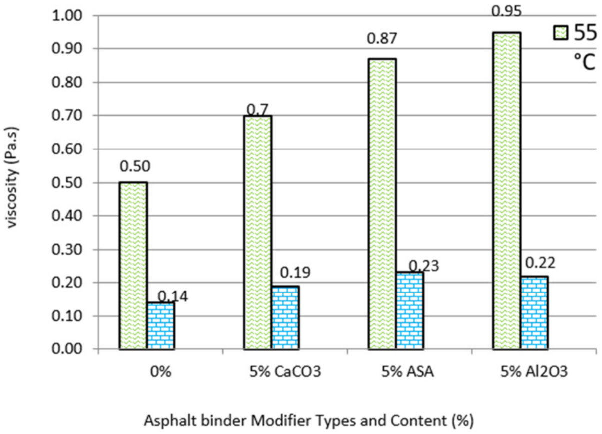

Fig. 3. Viscosities of base and modified asphalt binders.

D. Storage Stability

A binder has good storage stability properties if the difference in the softening point temperatures between the lower and upper test sections is less than or equal to 2.5 °C. Figure 4 shows that all the binders examined had a temperature difference of less than 2.5 °C. Therefore, it is evident that all the binders will exhibit good compatibility, good workability properties, and stable storage during high temperatures. Moreover, nanoparticles have more compatibility with the binder compared to the polymer, which might be due to the particle size of the nanomaterials.

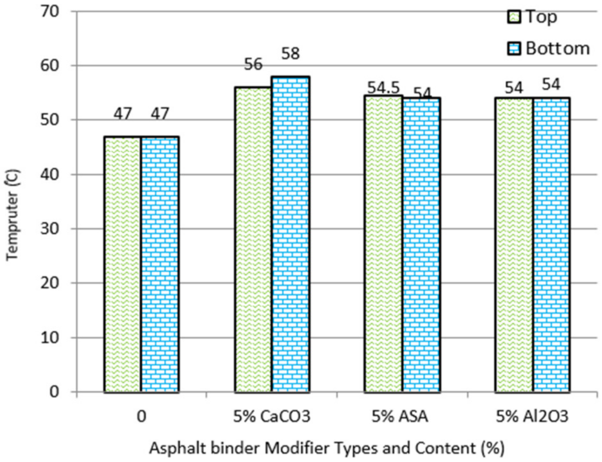

Fig. 4. Storage stability of base and modified binders.

E. Effect of Modifiers on Rheological Properties of Binders (Isochronal Plot of Complex Modulus and Phase Angle)

The isochronal plot can be used to determine the viscoelastic properties of the different binders when evaluated over a set of temperature ranges at a specific frequency. The isochronal plots of the complex modulus in Figure 5 were created using the complex modulus (G^*) and the temperature (°C) at a reference frequency of 1.592 Hz. As expected, there was a general reduction in the G^* value for all the corresponding binders with an increase in test temperature. All the G^* values of the modified binders superseded those of the base binder. In incremental order, the binder containing 5% $CaCO_3$ performed better than the base binder, followed by the binders with 5% ASA and 5% Al_2O_3. The 5% Al_2O_3 binder had the highest G^* values, indicating that it has the greatest tendency to resist the applied stresses acting on it before failure. This means that when used in the construction of asphalt pavements, it will exhibit better resistance to rutting compared to the other binders.

The phase angle is the time lag between the applied stress and the corresponding strain. This curve is particularly helpful in understanding the viscoelastic properties of the binder and also indicates the mechanical loss. In a perfectly elastic body, there is no time delay (zero) when there is an applied load, but a highly viscous binder will have a large phase angle value approaching 90 °C. Figure 6 shows the phase angle of the binders tested. The base binder had the greatest time delay when subjected to stress, indicating its low elasticity. Although the different binders had some degree of elasticity when subjected to stresses, the binder with 5% Al_2O_3 had the lowest phase angle values, which is an indication that it is the most elastic among the binders tested.

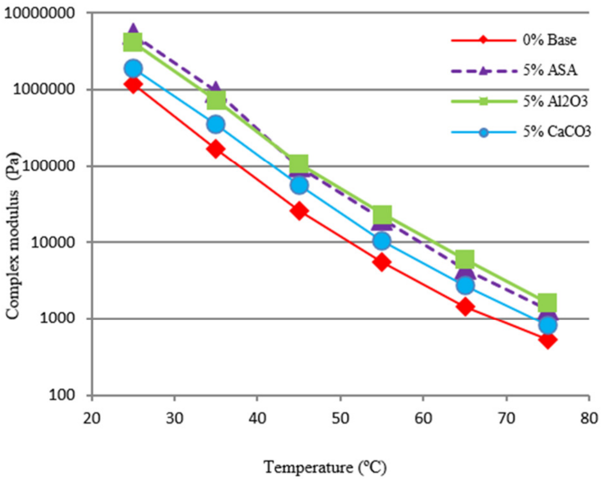

Fig. 5. Isochronical plot of complex modulus A for the binders.

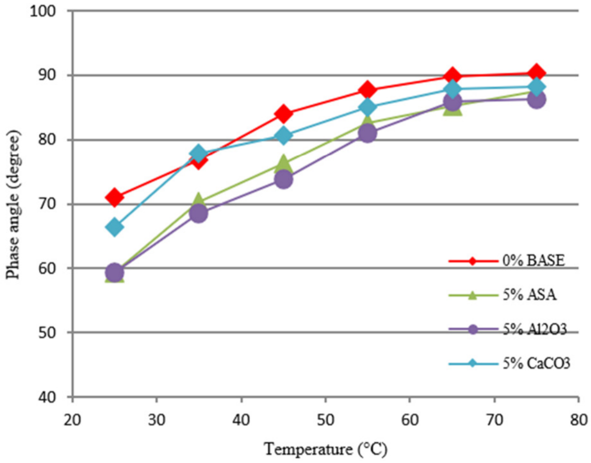

Fig. 6. Isochronal plots of phase angle at 1.5 Hz for the binders.

F. Rheological Master Curve

The master curves for the different binders were constructed to establish the relationship between the complex modulus and the reduced frequencies under multiple temperatures and times. A reference temperature was adopted to construct the master curve, while adjustments were made to other temperatures to achieve a single continuous smooth curve. This curve can be used to predict the binder stiffness and its properties at any given temperature. Figure 7 shows the master curves for asphalt binders examined. The base binder had the lowest complex modulus to reduced log ratio. In descending order, the 5% $CaCO_3$ binder performed better but was less to the base in resisting stresses than the 5% Al_2O_3 and 5% ASA binders, respectively. The binder with 5% Al_2O_3 had the greatest tendency to resist permanent deformation.

G. Rutting Parameter

To determine the rutting characteristics of the base and modified asphalt binders, the $G^*/\sin(\delta)$ was plotted at temperatures of 45, 55, 65, and 75 °C as specified by the Strategic Highway Research Program (SHRP). Figure 8 shows that the lowest value of $G^*/\sin(\delta)$ was recorded by the base binder, followed by 5% CaCO3. Although the $G^*/\sin(\delta)$ values recorded for the 5% ASA and the 5% Al_2O_3 binders were closely matched, the latter had the highest value closely followed by the former. The binder containing 5% Al_2O_3 has the greatest ability to resist permanent deformation and the greatest toughness at high temperatures. All modified binders had a $G^*/\sin(\delta)$ exceeding 1000 Pa at 70 °C. Furthermore, the high values obtained for the complex shear modulus of the nanomodified binders indicated their ability to absorb large stresses by dissipating applied forces during high and intermediate temperatures, thereby providing good rutting and fatigue resistance.

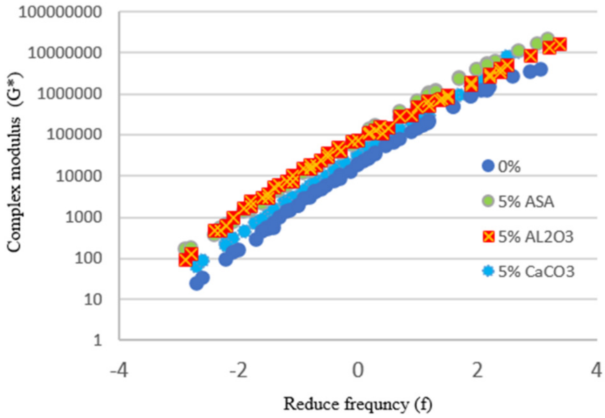

Fig. 7. Complex modulus master curve for base and modified binders.

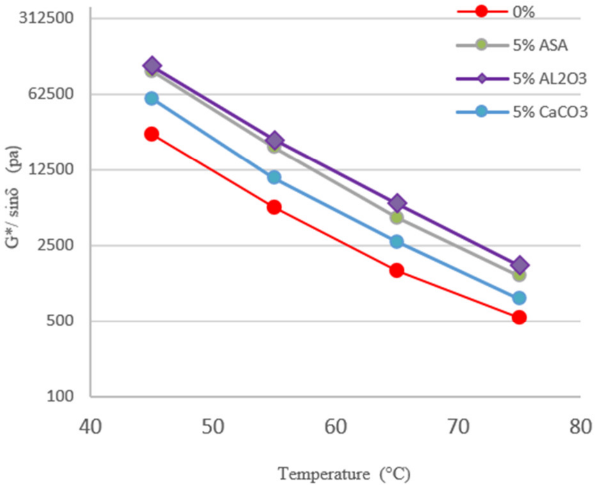

Fig. 8. Effect of temperature on the rutting parameter of base and modified asphalt binders.

H. Fatigue Parameter

To determine the fatigue parameter of bitumen at intermediate temperatures, the Superpave stipulates a maximum value of 5000 kPa described by the formula $G^*\sin(\delta)$. This demonstrates the better performance of the modifiers in resisting fatigue at intermediate temperatures. Figure 9 shows that at 35 °C, the base and the 5% $CaCO_3$ binders failed to meet the required minimum.

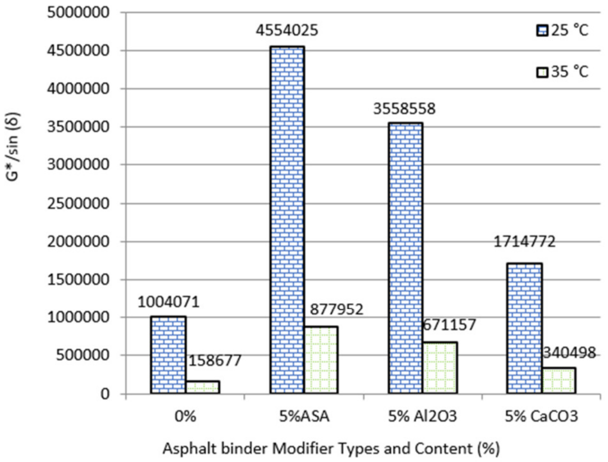

Fig. 9. Effect of temperature on fatigue parameter of base and modified asphalt binders.

I. *Failure Temperature*

According to the SuperPave specifications, the failure temperature of an asphalt binder is the point where the value of $G^*/\sin(\delta)$ falls below 1000 Pa. These are the criteria adopted in determining the performance grade of asphalt binders [22]. The results in Figure 10 indicate that the lowest failure temperatures were recorded by the base binder followed by the 5% $CaCO_3$ with temperatures of 69 and 74 °C, respectively, which indicates that they are more sensitive to temperature. The other modified binders, namely 5% ASA and 5% Al_2O_3, had higher failure temperatures of 77 and 78 °C, respectively, and showed less sensitivity when compared to the base asphalt.

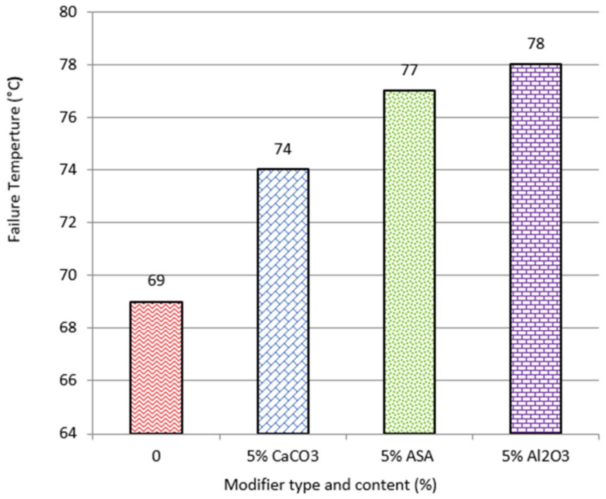

Fig. 10. Failure temperatures of unmodified and modified binders.

IV. CONCLUSION

This study compared three commonly used binder modifiers, ASA, Al_2O_3, and CaCO3, with the base binder. Concerning the physical properties of the binder, it has been shown that, in general, polymers and nanomaterials decrease the penetration of bitumen binders, which, on the other hand, leads to higher softening points and viscosity values. The results of the storage stability tests showed that all modified binders maintained a stable form after storage at high temperatures. When considering the rheological effects, properties such as rutting resistance at high temperatures, cracking resistance at low temperatures, and performance improved massively when introducing these modifiers. From the rutting values obtained, it is evident that the binder with 5% Al_2O_3 nanoparticles had the highest ability to resist permanent deformation and the highest toughness at high temperatures. The 5% ASA polymer binder exhibited the greatest strength under thermal cracking from the isochronal plot. The 5% ASA and 5% Al_2O_3 binders had higher failure temperatures compared to the base asphalt and 5% $CaCO_3$ binders. The use of polymers and nanomaterials has proven to be very important in the performance and durability of asphalt pavements by modifying the physical and rheological properties of the binders. Utilizing nanomaterials has proven to yield better properties when used as a modifier in asphalt binders, but their use is limited due to their uniquely complex production and subsequent use in experimental research.

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