

Evaluation of elevated temperature properties of asphalt cement modified with aluminum oxide and calcium carbonate nanoparticles

Shaban Ismael Albrka Ali^{1,2}, Amiruddin Ismail², Ramez A AlMansob³ and Dhawo Ibrahim Alhmali²

¹Civil Engineering Department, Near East University, Near East Boulevard, 99138 Nicosia, North Cyprus, Mersin 10, Turkey

²Department of Civil and Structural Engineering, Universiti Kebangsaan Malaysia, Pekan Bangi, 43600 Bangi, Selangor, Malaysia

³Faculty of Engineering, Technology and Built Environment, UCSI University, 56000 Cheras, Kuala Lumpur, Malaysia

E-mail: shabanismael.albrka@neu.edu.tr, shabarofking10@gmail.com

Abstract. Higher temperature properties of the asphalt cement have been characterized before and after modification using dynamic shear rheometer (DSR) and viscosity testing. In this study, calcium carbonate nanoparticles (CaCO_3) and aluminum oxide nanoparticles (Al_2O_3) have been added to the base asphalt cement with concentrations of 3, 5 and 7%.wt by the weight of the asphalt cement. The increase of CaCO_3 and Al_2O_3 content has significant effect on the properties of asphalt cement. The viscosity of the modified asphalt cement increased up to 90 and 108% respectively compared to the base asphalt cement. In addition, the results showed that both modifiers have great storage stability and compatibility at elevated temperature. The evaluation of the rheological properties of asphalt cements revealed that the stiffness of the modified samples improved with additional increase of the modifier concentration of up to 5%, which indicates better resistance to rutting parameter. The enhancement was up to 388.89% for Al_2O_3 and 74.07% for CaCO_3 . As a result, the usage of CaCO_3 and Al_2O_3 nanoparticles can be considered as appropriate alternative materials to modify asphalt cement.

1. Introduction

Asphalt cement has been used for many years in the construction of highways and road networks. Therefore, it is able to resist the distresses caused by traffic loads and change in temperatures [1]. However, due to the limitation of temperature susceptibility, the low, intermediate and high temperature and temperature performance of asphalt need to be enhanced. As a result, modification of asphalt cement is crucial to improve the performance of pavement [2-5]. There are numerous types of asphalt cement modifiers, such as polymers, nanomaterials and rubbers. Currently, nanomaterials have been rapidly incorporated into the field of asphalt cement with various types of nanomaterials being used as modifiers of asphalt cement and asphalt mixes. It was found that nanomaterials are able to improve the performance of asphalt cement and asphalt mixes. A study conducted by Wang et al. (2017) showed that the performance investigation demonstrated that multi-walled carbon nanotubes



(CNTs) performed a positive role to enhance the properties of modified asphalt cements. In addition, the anti-aging and workability properties of modified asphalt cements were significantly improved [7]. Moreover, Ezzat et al. (2016) performed a research focusing on the influence of using nanosilica and nanoclay as modifiers of asphalt cement. From the results, it was noted that the penetration value decreased while the softening point and viscosity increased. The addition of increasing amount of both modifiers led to the increase in the high-performance grade of the modified asphalt cements and the rutting parameter [8]. The main aim of this study is to investigate and compare the influence of Al_2O_3 and CaCO_3 on the properties of base asphalt cement at high temperatures. In addition, the study compares the Superpave rutting specification ($G^*/\sin \delta$) with Aroon Shenoy parameter ($G^*/(1-(1/\tan \delta \sin \delta))$).

2. Experimental design

2.1. Materials

The base asphalt cement used in this study was 60/70 penetration grade, supplied by the factory at Port Klang Malaysia. The nanomaterials used were aluminum oxide nanoparticles (Al_2O_3) and calcium carbonate nanoparticles (CaCO_3) in white powder form supplied by the factory of the Shijiazhuang Chanchiang Corporation company in China. The physical properties of the base asphalt cement and nanoparticles are shown in Table 1.

Table 1. The physical properties of the asphalt cement and nanoparticles.

Material	Properties	Test Method	Value
Asphalt cement 60/70	Specific Gravity	ASTM D70	1.30
	Penetration @ 25 °C	ASTM D5	70
	Softening point (°C)	ASTM D36	47.0
	Viscosity @ 135 °C (Pa.s)	ASTM D4402	0.5
	Ductility (cm) @ 25 °C	ASTM D113	≥100
CaCO_3	Density	-	2.70
	Size	nm	40
	Form	-	Powder
Al_2O_3	Density	-	-
	Size	nm	13
	Form	-	Powder

2.2. Preparation of Al_2O_3 CaCO_3 Modified Asphalt Cement

The base asphalt cement was heated until it became fluid and stirred for about 10 min at the temperature of 170 °C. Then, three different percentages of both nanoparticles (Al_2O_3 and CaCO_3) at 3, 5 and 7% by the weight of the asphalt cement (%wt) were added regularly into the base asphalt cement under the high shear mixture speed of 5000 rpm for 90 min until it realized a homogenous asphalt cement blend for each percentage.

2.3. Testing procedures

This section describes the tests conducted in the laboratory to evaluate the influence of both modifiers on the base asphalt cement.

2.3.1. Viscosity. The Brookfield Rotational Viscometer was used for the assessment of the viscosity of the base asphalt cement, Al_2O_3 and CaCO_3 modified asphalt cement samples. Three readings were recorded for each test, and the average reading was accepted as the test result. The test temperatures were 135 °C and 165 °C respectively.

2.3.2. Storage Stability Test. The base asphalt cement and the modified asphalt cement were poured into an aluminum foil tube with the height of 16 cm and width of 3 cm. The foil tubes were closed and stored vertically at a temperature of 163 ± 5 °C in an oven for 48 hours. Therefore, the samples were cooled and divided horizontally into three sections. The storage stability samples were taken from the top and bottom sections and the softening points of the sections were determined. If the difference between the top and the bottom sections was less than 2.5 °C, then the sample was considered to have great high-temperature storage stability. If the softening points differed by more than 2.5 °C, then the sample was considered to be unstable [8, 9].

2.4. Dynamic Shear Rheometer (DSR)

Dynamic Shear Rheometer (DSR) is used to determine the rheological properties of asphalt cements, including complex shear modulus (G^*) and phase angle (δ) at various temperatures and frequencies. These parameters are able to describe the viscoelastic behavior of asphalt cement. The G^* (complex shear modulus) and δ (phase angle) of asphalt cement are extremely dependent on the test temperature and frequency of loading. G^* (complex shear modulus) is a measure of the total resistance of a material to deformation when exposed to a sinusoidal shear stress load. G^* consists of both elastic and viscous components. The δ (phase angle) is an indicator of the relative amounts of viscoelastic mechanisms. In this study, the DSR test investigated the high temperature properties of Al_2O_3 and CaCO_3 nanoparticles modified asphalt cement using a frequency sweep test. The frequency sweep applied was 0.159 to 15 Hz and the temperature was from 45 °C to 75 °C. The plate used in the test was a 25 mm diameter spindle with a gap of 1 mm.

3. Results and discussion

3.1. Rotational Viscosity

Figure 1 shows the results of the viscosity of the asphalt cement samples which were measured using the Brookfield viscometer at 135 °C and 165 °C. It was noted that the increase of both nanoparticles in the base asphalt cement led to the increase of viscosity. Moreover, the base asphalt cement had the lowest viscosity among the blends, while 7% Al_2O_3 had the highest viscosity. Figure 1 also indicates that the viscosity of the base asphalt cement and the modified asphalt cements within the specifications of the Superpave™ Standard required limit at 135 °C was less than 3 Pa.s. In addition, asphalt cements modified with Al_2O_3 nanoparticles showed higher viscosity value than modified samples with CaCO_3 nanoparticles. This indicates that Al_2O_3 nanoparticles show better resistance to rutting parameter. The highest viscosity leads to the highest mixing and compaction temperatures and the lowest value leads to lowest mixing and compaction temperatures.

3.2. Storage stability of CaCO_3 and Al_2O_3 nanoparticles modified asphalt cement

The difference between the top and the bottom sections of the softening point of the base and modified asphalt cement indicates its storage stability. The less the difference between the sections indicates better storage stability for asphalt cements [10, 11]. Figure 2 shows the results of storage stability of the base asphalt cement, and CaCO_3 and Al_2O_3 nanoparticles modified asphalt cement. It was found that the differences of the softening points for modified asphalt cements were 1 °C and less. Therefore, the entire asphalt cements passed the requirement value of storage stability as the differences were less than 2.5 °C for all asphalt cement samples. This indicates that CaCO_3 and Al_2O_3 nanoparticles modified asphalt cements are stable and are able to be stored at high temperatures.

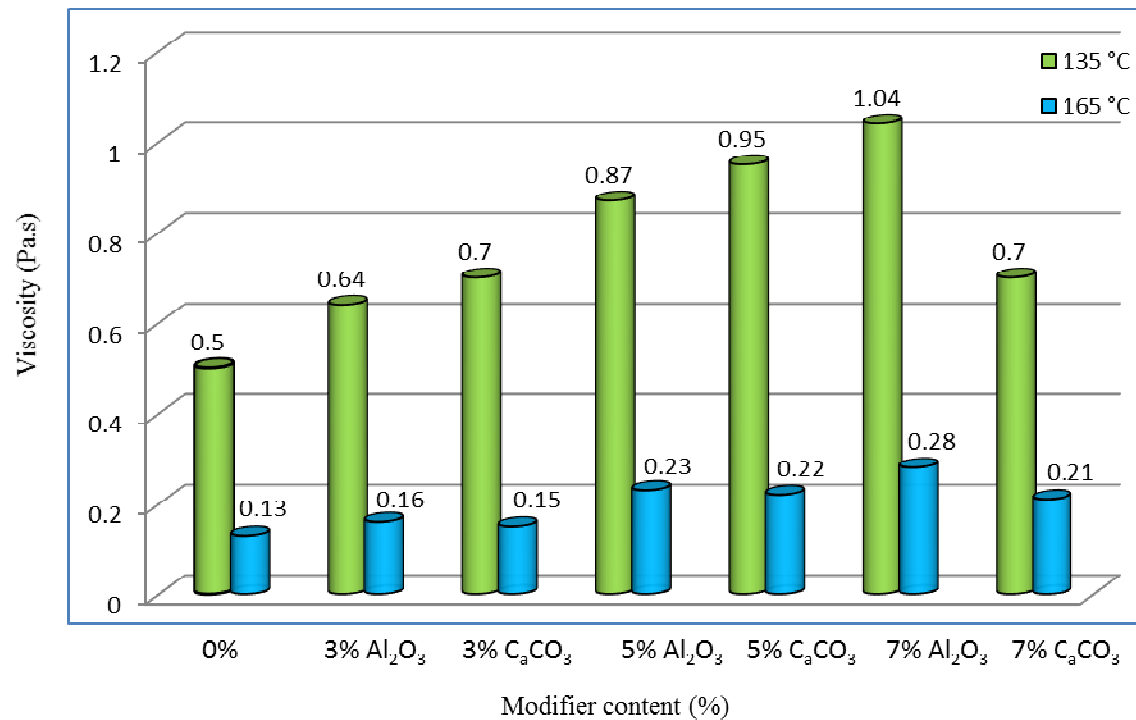


Figure 1. Viscosity of base and modified asphalt cement at 135 °C and 165 °C.

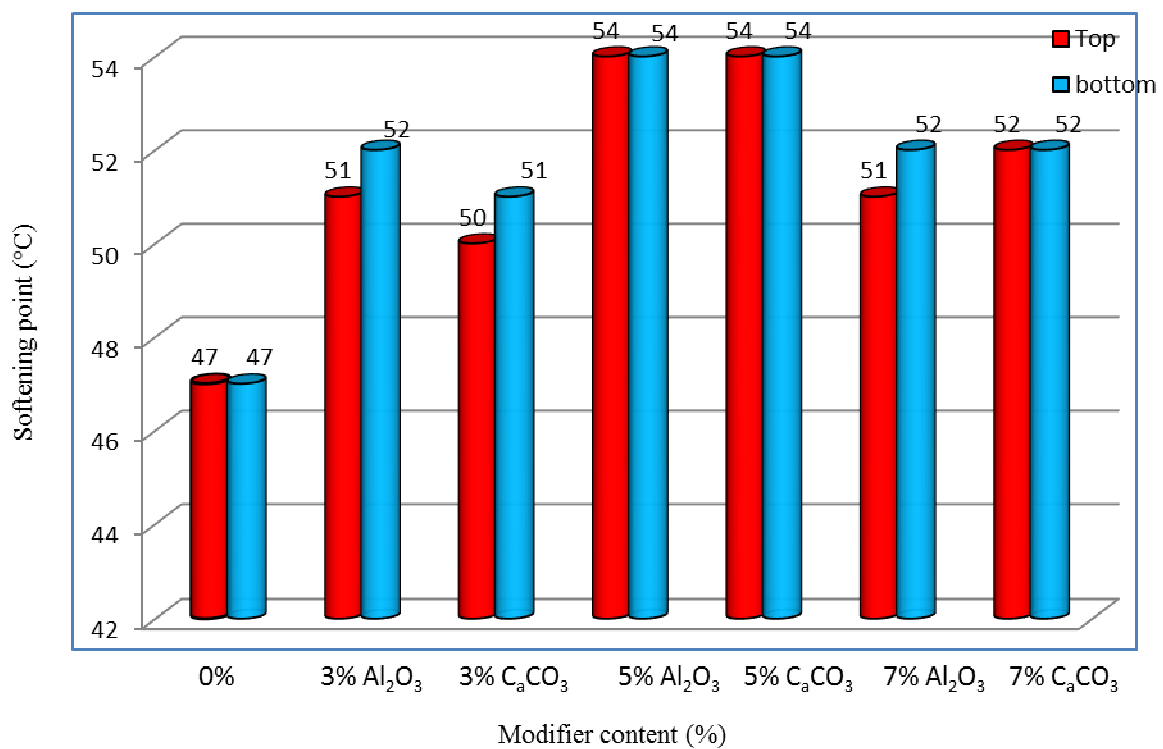


Figure 2. Storage stability of the base and modified asphalt cements.

3.3. The Dynamic Shear Rheometer (DSR)

3.3.1. Isochronal Plots. According to the compatibility between asphalt cement and the modifier, the modification of asphalt cement may result in two types of blends. The first type is a heterogeneous blend, in which the modifier and asphalt cement are incompatible and lead to two separate phases. The second type is a homogeneous blend, in which the modifier and asphalt cement are quite compatible [11]. Figure 3 shows the isochronal plots of the modified asphalt cements. It was observed that the increase of modifiers content caused an increase in the stiffness of the modified asphalt cements, regardless of the temperatures. Moreover, it was noted that the samples modified with Al_2O_3 nanoparticles had higher complex shear modulus value compared to those modified with CaCO_3 nanoparticles. This suggests that the Al_2O_3 nanoparticles have higher resistance to permanent deformation. Both modifiers at 7% showed different behaviour as the complex shear modulus was reduced. This may be due to the agglomeration among the nanoparticles with additional increase of modifier in asphalt cement blends.

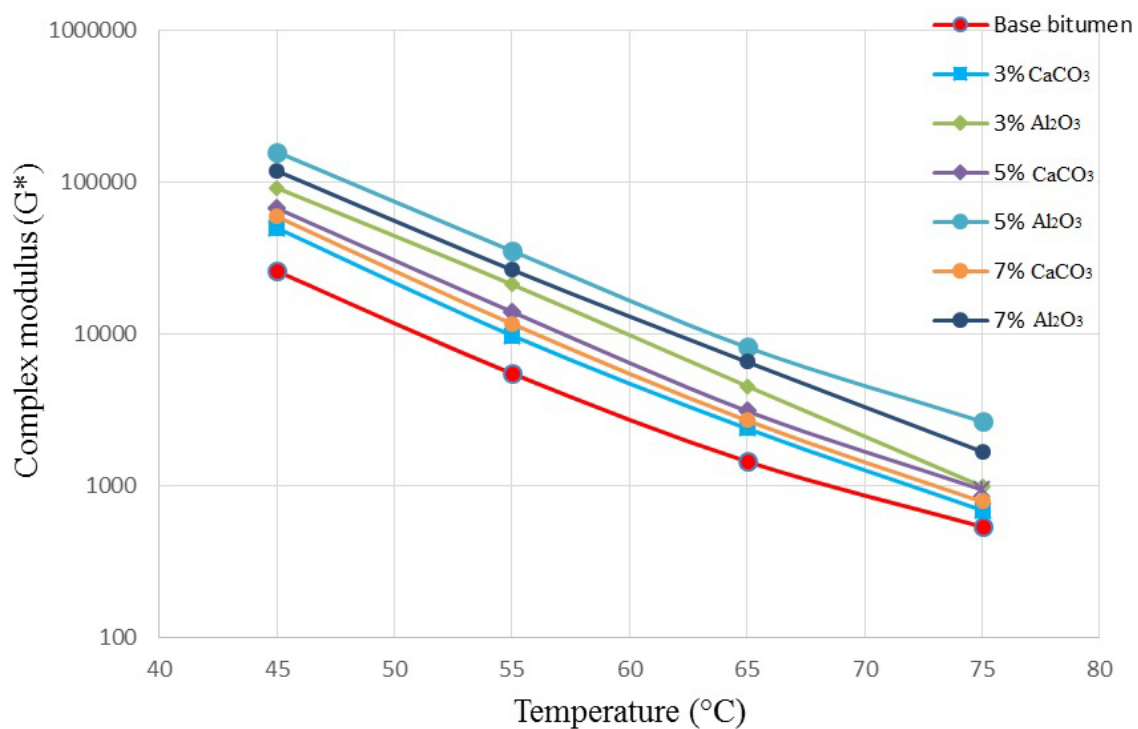


Figure 3. Isochronal plots of base and modified asphalt cements.

3.3.2 Rutting Parameter. The Superpave method requires $G^*/\sin\delta = 1$ kPa as the minimum of SHRP rutting parameter for unaged samples of asphalt cement. Figure 4 shows that the lowest rutting value was displayed by the base asphalt cement, while the modified asphalt cement with Al_2O_3 nanoparticles displayed the highest value among the blends. The higher $G^*/\sin\delta$ depicts asphalt with better rutting resistance. Therefore, these results prove that Al_2O_3 nanoparticles modified asphalt cement performs much better than CaCO_3 nanoparticles modified samples in rutting performance. However, the 7% samples showed different behavior as the value of $G^*/\sin\delta$ decreased slightly. Overall, it can be observed that all asphalt cements had $G^*/\sin\delta$ values that were larger than 1.0 kPa at 65 °C. The complex shear modulus (G^*) and phase angle (δ) at high elevated temperatures were proven as indicators of the rutting susceptibility of the asphalt ($G^*/\sin\delta$) and the limitation was identified to be $G^*/\sin\delta = 1$ kPa as the minimum value according to Superpave specification. Aroon Shenoy suggested

the term $G^*/(1-(1/\tan\delta \sin\delta))$ as a refinement of the Superpave specification parameter $G^*/\sin\delta$. Figure 4 shows the evaluation of the rutting parameter of the base and modified asphalt cements with nanoparticles using the Superpave specification (SPS) and the Aroon Shenoy parameter (ASP) methods. From the results, it was observed that there were no significant differences between the two techniques. This indicates that both methods are able to evaluate and determine the rutting parameters of modified asphalt cements.

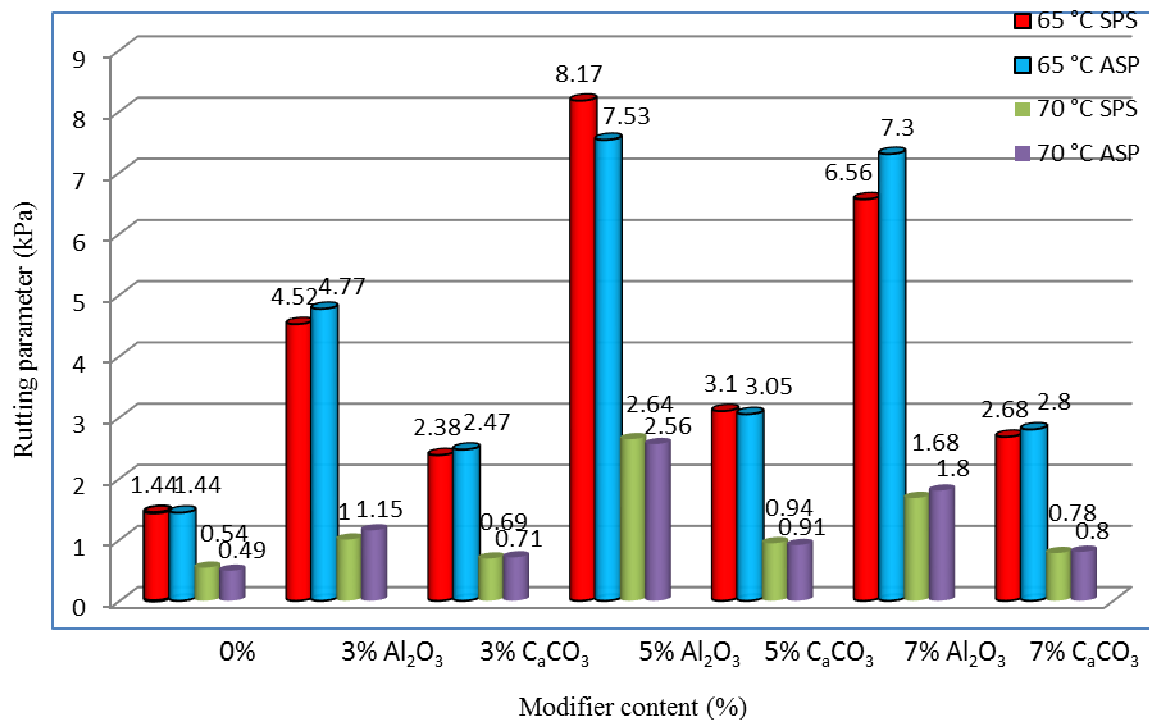


Figure 4. Evaluation of rutting depth of base and modified asphalt cements using SPS and ASP.

4. Conclusions

In this study, the effects of introducing Al₂O₃ nanoparticles and CaCO₃ nanoparticles modified asphalt cements were investigated and the high temperatures rheological properties of the modified asphalt cements with both modifiers were also evaluated. The results indicated that the modified asphalt cements showed greater stiffness at elevated service temperatures. It was also found that the rutting influence of the modified asphalt cements with Al₂O₃ and CaCO₃ nanoparticles was less than the base asphalt cement, and the improvement of the modified samples was up to 4.6 and 1.4 times respectively compared to the base asphalt cement. This indicates higher performance of modified samples at high temperatures. Moreover, the investigation approved that both Superpave and Aroon Shenoy parameters are able to evaluate the permanent deformation of modified asphalt cement. The evaluation of rheological examinations indicated that the concentrations of 5% Al₂O₃ and 5% CaCO₃ can be considered as the best performance condition of the asphalt cement for both modifiers and was selected as the optimum content of modifiers.

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