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Impact of Fly Ash-Based Geopolymer Modification on the High-Temperature Properties of Bitumen

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***Abstract*—**This study evaluated the mechanical and rheological performance of fly ash-based geopolymer at high temperatures. A series of laboratory tests were conducted on neat bitumen and three modified bitumen samples, which incorporated fly ash-based geopolymer at various percentages. Low-calcium fly ash was used as the alumina-silica source. The dynamic shear rheometer and rotational viscometer were employed to determine high-temperature properties, while conventional tests such as penetration and softening point were used to evaluate the physical properties of bitumen. Short-term aging resistance of the samples was assessed using the rolling thin film oven. The results show that geopolymer has a compromising effect on bitumen properties, with improved stiffness, enhanced mechanical strength, and increased thermal susceptibility of the asphalt binder.

***Keywords*—**Bitumen, geopolymer, rutting, dynamic mechanical analysis.

I. INTRODUCTION

BITUMINOUS binders have been widely used in the construction industry for many years in various applications. Bitumen, which is obtained by distillation of crude oil, can be found in viscous or semi-solid form. Although bitumen has been used as an insulation material for roofs [1] and as a waterproofing agent [2], its primary use is as a binder together with aggregates in the production of asphalt coatings for road construction [3]. Asphalt concrete performance is primarily governed by the structural characteristics of bitumen, which accounts for approximately 5-7% by weight and 15-17% by volume of the mixture, as widely recognized [4].

Asphalt pavements are exposed to various environmental and traffic loads such as humidity, temperature, and precipitation during their service life. These factors significantly alter the structural properties of the bitumen binder over time, leading to deformations such as thermal and fatigue cracks, and rutting, which considerably reduce the performance of the asphalt pavement [5]. Such deformations occur primarily due to the loss of structural strength of the bituminous binder over time, which was initially predicted during the design phase and is caused by traffic loads and temperature. To mitigate these issues, researchers have focused on modifying the bitumen by adding various additives such as polymers [6], fibers [7], wastes [8], etc., to enhance its structural and rheological properties and minimize the deformations mentioned above.

The increasing focus on sustainable transportation policies has led to a rising demand for bitumen modifiers that not only improve asphalt performance but also promote environmentally friendly and sustainable practices [9]. Within this context, geopolymerization is a promising solution for managing alumina-silica based waste and providing a new avenue for their recycling in asphalt applications [10].

Geopolymerization is the reaction of a solid aluminosilicate with a highly concentrated aqueous solution of alkali hydroxide or silicate, which forms synthetic alkali aluminosilicate, an inorganic polymer known as geopolymer [11]. A large number of studies have reported that geopolymer production does not necessitate calcination at high temperatures [12], [13], so it is possible reduce emission by about 80% [14]-[16]. Research up to now showed that numerous aluminosilicate sources such as metakaolin [17], red mud [18], rice husk [19] can be used in the geopolymer mortar production.

This study is primarily aimed at characterizing the mechanical and rheological performance of Fly Ash-based geopolymer (FAG) at moderate and high temperatures. To achieve this goal, a series of systematic laboratory tests were conducted on both neat and three modified bitumen samples, which incorporate FAG at various percentages (5%, 10%, 15%). Low calcium fly ash (Class F) was considered as the alumina silica source. To determine high temperature properties, the dynamic shear rheometer (DSR) and rotational viscometer (RV) were employed, while conventional tests such as penetration and softening point were utilized to evaluate conventional properties of bitumen samples. conducted. Additionally, rolling thin film oven (RFTO) was utilized to investigate the short-term aging resistance of FAG modified bitumen samples.

II. MATERIALS AND METHOD

A. Properties of Bitumen and Geopolymer

The neat bitumen used in this study was 50/70 penetration grade with a specific gravity of 1.035, obtained from the Turkish Petroleum Refineries Corporation Izmir, Turkey. The characterization of the bitumen was carried out using conventional tests including penetration, ductility, softening point, and Brookfield viscosity, in accordance with the relevant ASTM standards (Table I).

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TABLE I
CONVENTIONAL CHARACTERISTICS OF NEAT BITUMEN

Test	Unit	Specification	Value
Penetration	mm^{-1}	ASTM D5	62
Softening Point	°C	ASTM D36	47
Ductility	cm	ASTM D113	>130
Viscosity at 135°C	Pa.s	ASTM D4402	0.41
Viscosity at 165°C	Pa.s	ASTM D4402	0.11

The F-class FA was used as the raw material for the geopolymerization process, with NaOH-Na_2SiO_3 alkali solution serving as the activator. The activator was prepared with a 1.0 MS ratio, which represents the SiO_2 percent/Na_2O percent in the alkaline solution. The SiO_2 percentage was calculated by taking into account the amount of SiO_2 entering the mixture from Na_2SiO_3, while the Na_2O percentage accounted for both the amount of Na_2O from Na_2SiO_3 and NaOH. To prepare the activator, the necessary amount of NaOH and Na_2SiO_3 were added to 1-liter containers and mixed for 45 minutes at 500 rpm, followed by hand shaking for 5 minutes (Fig. 1 (a)). The mixture was then allowed to rest for 24 hours. The geopolymer mortar was placed in molds of 30 mm × 30 mm × 30 mm and cured at ambient temperature for 24 hours and then in an oven at 60 °C for 3 days and were ground with a RETSCH PM 100 brand ball mill until the whole size would pass under the No:200 (0.0075 mm) sieve (Figs. 1 (b)-(d)).

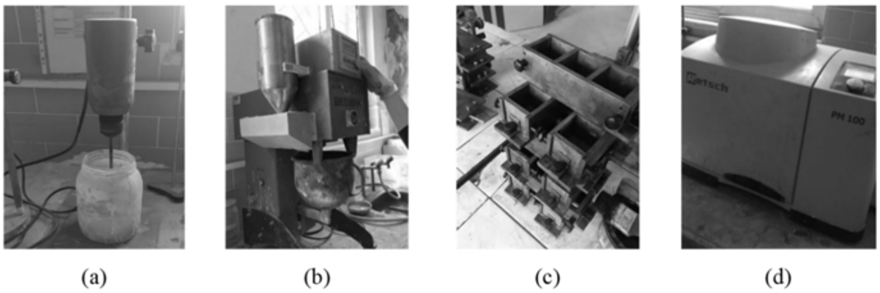

(a) (b) (c) (d)

Fig. 1 Geopolymerization procedure: (a) preparing alkaline activator (b) preparing mortar (c) molding (d) grinding

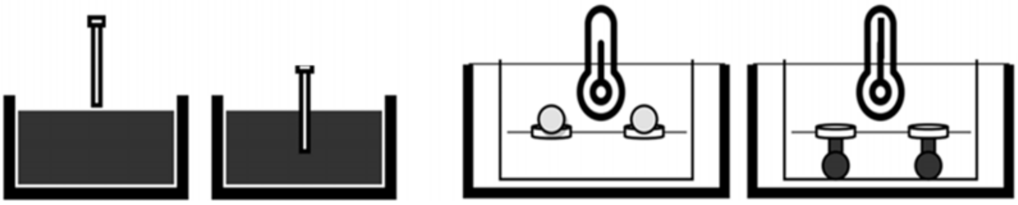


Fig. 2 Illustration of (a) penetration and (b) softening point tests

The addition of FAG powder to the neat bitumen was achieved through a SILVERSON L5M high-speed mixer at rates of 5%, 10%, and 15% by weight. The mixing process was carried out for 45 minutes at 150 °C and a shear rate of 2500 rpm.

B. Mechanical Tests

Mechanical and physical properties of both virgin and modified binders were determined by penetration and softening point tests. Penetration tests were conducted in accordance with ASTM D5 [20] to analyze hardness and consistency of the virgin and modified asphalt using a standard 100 g needle at 25 °C. Softening point test was conducted according to ASTM D36 [21] to determine the temperature at which bitumen softens without deteriorating its chemical form with two certain sized rings and steel balls. Schematically illustration of penetration and softening point tests are given in Figs. 2 (a) and (b), respectively.

C. Short-Term Aging

As per the ASTM D2872 standard, samples of 35 grams with a precision of 0.5 grams are carefully placed in 8 glass bottles and subjected to the RTFO procedure. The glass bottles are arranged horizontally in the rotary oven at a temperature of 163 °C, and the turntable is rotated at a speed of 15 rpm, causing the flowing bitumen to spread and form a thin film on the bottle's surface. The test is carried out for a period of 85 minutes while the binder samples are continuously sprayed with air at a rate of 4000 ± 200 ml/minute. This results in the oxidation of the bitumen samples due to the combined influence of air and temperature. After the test, the samples are reweighed, and the percentage of mass loss is calculated based on the initial and final weights.

D. Dynamic Mechanical Analysis

The dynamic mechanical analysis (DMA), as described in AASHTO T315 [22], is utilized to determine the complex modulus (G^*) and phase angle (δ) of bitumen, which are essential in calculating high-temperature performance criteria. During dynamic mechanical analysis, the bottom plate is stationary, while the upper plate oscillates at an angular frequency of 10 rad/sec or 1.59 Hz, with a 1 mm gap between the 25 mm parallel plates. The rheometer measures the maximum stress, resultant strain, and the lag between these two parameters. In this study, DMA was performed on both neat and modified bitumen's using Anton Paar SmartPave DSR device to obtain the complex modulus G*, δ, and rutting factor (G*/sinδ).

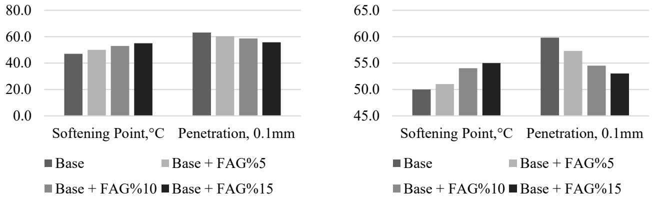
It should be noted that as per the Strategic Highway Research Program (SHRP) guidelines, the (G*/sinδ) value of bitumen at Superpave performance grading (PG) temperature must meet or exceed 1 kPa for unaged specimens and 2.2 kPa for short-term aged specimens to be suitable for use in HMA.

E. Mixing and Compaction Temperatures

The Brookfield RV was used to determine the viscosity values of both neat and modified bitumen samples at 135 °C and 165 °C, following the guidelines outlined in ASTM D 4402. For the test, 8-11 grams of bitumen sample were weighed and transferred into the sample container. The container was then placed into the Brookfield RV device, which had been pre-conditioned at 135 °C for 30 minutes. During the test, the viscosity values were determined by measuring the torque applied by the cylindrical tip (spindle) immersed in the bitumen at 135 °C and 165 °C to maintain a constant rotation speed of 20 rpm. Note that, the optimum viscosity range for bituminous binders during mixing and compaction is reported to be 0.17 ± 0.02 Pa.s and 0.28 ± 0.03 Pa.s, respectively.

III. RESULTS AND DISCUSSION

As previously mentioned, the neat binder was enhanced with various proportions of FAG to examine the potential of FAG as an additive for asphalt binders. Fig. 3 illustrates the outcomes of the penetration and softening point tests conducted on the base and modified asphalt samples. It should be noted that the modified binder specimens were labeled as FAG5%, FAG10%, and FAG15%.



(a) (b)

Fig. 3 Penetration and Softening Point test results of (a) unaged (b) short term aged binders

Upon examining Fig. 3 (a), it is evident that the incorporation of FAG enhances the stiffness of the base binder, leading to higher softening point and lower penetration values. This trend becomes more pronounced after subjecting the samples to short-term aging. The correlation between these properties is indicative of the temperature susceptibility of the bitumen. The temperature susceptibility of both the base and modified binders was evaluated by computing the penetration index (PI) [23]. Fig. 4 illustrates the variation of PI values for both unaged and short-term aged samples.

The PI value provides an indication of the susceptibility of the binder to temperature changes, with a positive value indicating lower susceptibility. All of the FAG modified binder samples in this study met the required specifications outlined in a previous study [24] with PI values ranging from -1 to +1. Fig. 3 illustrates a clear increase in PI with increasing FAG content in the binder, indicating improved resistance to temperature fluctuations with the addition of FAG.

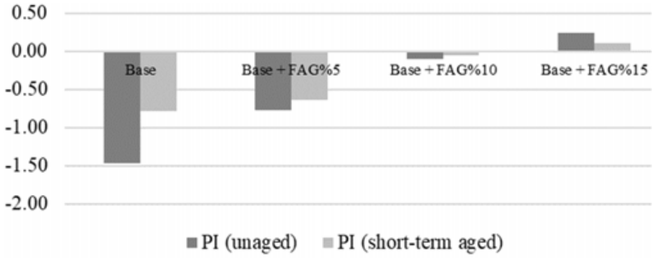


Fig. 4 The change of PI values for unaged and short-term aged binder samples

Moreover, it was observed that the PI values of the short-term aged and unaged binder samples became closer as the FAG content increased, suggesting enhanced aging resistance with the addition of FAG. This was further supported by the mass loss measurements, which showed values of 0.38%, 0.36%, 0.36%, and 0.35% for the base, FAG5%, FAG10%, and FAG15% modified binders, respectively, before and after the short-term aging process.

Fig. 5 displays log-viscosity versus temperature plots for each binder. From a practical standpoint, the RV test results conducted on both the base and FAG-modified bitumen samples at 135 °C and 165 °C indicate that an increase in the proportion of FAG additive did not significantly change or substantially reduce both mixing and compaction temperatures. As seen in Table II, viscosity values of base and FAG-modified samples are increased by increasing additive content at both 135 °C and 165 °C.

TABLE II
MIXING & COMPACTION TEMPERATURE RANGES OF BASE AND FAG-MODIFIED BINDERS

Binder	Mixing Range (°C)	Compaction Range (°C)
Base	155 - 157	143 - 145
Base + FAG5%	156 - 158	145 - 147
Base + FAG10%	155 - 157	143 - 144
Base + FAG15%	157 - 158	145 - 146

Moreover, at a higher temperature of 165 °C compared to 135 K°C, an increase in viscosity values was observed, which is hypothesized to be due to the migration of water molecules trapped within the geopolymer structure upward. These findings were also attributed to the steam pressure generated by the formation of bubbles within the geopolymer modified binder [16].

The complex modulus and phase angle factors were obtained from the dynamic mechanical test conducted at elevated temperatures. These rheological factors serve as indicators of the binder's viscoelastic behavior, which is directly related to its ability to resist rutting deformation. More specifically, G* is the resultant vector of the two components, namely the storage and loss modulus, and the phase angle represents the angle formed between G* and the horizontal axis. In general, a higher G* value with a lower δ is considered more desirable in terms of improved rutting resistance [25].

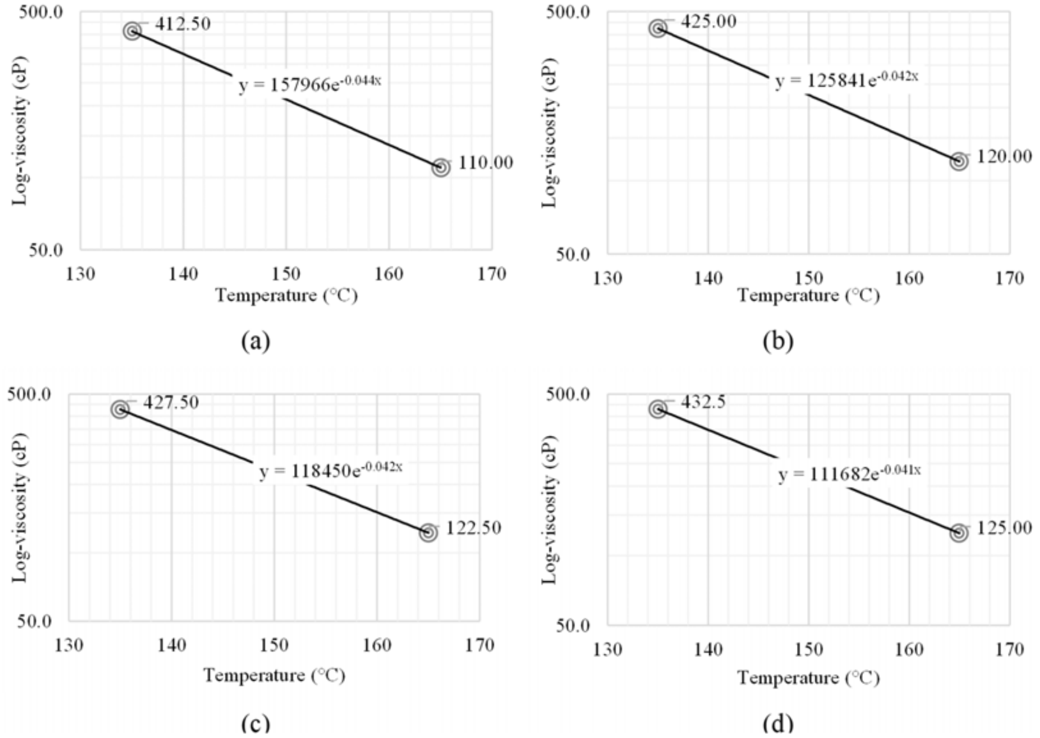


Fig. 5 Log-viscosity versus temperature (a) Base (b) Base + FAG5% (c) Base + FAG10% (d) Base + FAG15%

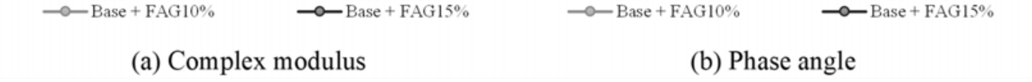


Fig. 6 Dynamic mechanical test results (a) Complex modulus (b) Phase angle

Fig. 6 clearly illustrates that the addition of FAG remarkably improves the G* value of the binder, with more pronounced improvement at 58 °C. However, at higher temperatures such as 70 °C, the G* values of the FAG-modified binder approaches to the base binder. This is because the binder becomes more viscous and the adhesive forces between the geopolymer and binder decrease. Consequently, the binder requires a lower sinusoidal stress as the base binder to achieve a specific deformation level, resulting in a higher δ value similar to that of the base binder.

In addition, when compared to commonly used polymers, the phase angle was found to be quite higher. This could indicate that FAG-modification has increased the binder's mechanical strength, while elasticity not changed significantly. Rosyidi et al. [15] indicated that there is no chemical interaction between geopolymer and bitumen. This means that the bitumen-geopolymer mixture may experience thermal segregation or separation at high temperatures, due to the absence of chemical bonding.

IV. CONCLUSION

This study evaluated the mechanical and high-temperature rheological properties of FAG-modified bitumen at three different modification ratios. Post-analysis revealed that the FAG additive had a compromising effect on bitumen properties, with improved stiffness, enhanced mechanical strength, and thermal susceptibility of the asphalt binder.

Based on the systematically conducted experimental procedure, it can be concluded that the optimal dosage of FAG in the modification is 10% by binder weight. From an R&D perspective, geopolymerization represents a sustainable and eco-friendly approach, particularly in the disposal of solid wastes with a rich aluminosilicate content, such as spent refractories, bauxite tailings, or other by-products.

Fly ash, a coal combustion residue from thermal power plants, was used as an aluminosilicate source in this study. However, the main challenge associated with using fly ash in geopolymer production is that it requires the use of alkali silicates with molar ratios of SiO_2:M_2O below 1.20 or alkaline solution systems based on pure NaOH (8M or 12M). This is because fly ash itself is not reactive enough to form geopolymer when used alone. The molar ratio of SiO_2:M_2O and the concentration of NaOH used in the alkali silicate solution play a critical role in the geopolymerization process and can affect the properties of the final geopolymer product. Therefore, the appropriate alkali silicate solution must be carefully selected and prepared to produce a high-quality geopolymer material using fly ash. For future studies, it is recommended to investigate composite usage of fly ash with an enriched silicate source in geopolymer production.

REFERENCES

[1] Obi, N.I., M.N. Razali, and A.H. Nour, The potentials of emulsified modified bitumen (EMB) for coating and insulation: An overview. Materials Today: Proceedings, 2022. 57: p. 1288-1295.

[2] Vollpracht, A. and W. Brameshuber, Environmental compatibility of bitumen waterproofing. Materials and structures, 2013. 46: p. 1257-1264.

[3] Katanalp, B.Y., et al., Atik Kömür Katkili Asfalt Betonu performans karakteristiklerinin yapay sinir ağları ve merkezi kompozit tasarım yöntemleri kullanılarak karşılaştırılması. Mühendislik Bilimleri ve Tasarım Dergisi, 2019. 7(3): p. 680-688.

[4] Hassanpour-Kasanagh, S., et al., Rheological properties of asphalt binders modified with recycled materials: A comparison with Styrene-Butadiene-Styrene (SBS). Construction and Building Materials, 2020. 230: p. 117047.

[5] Mohod, M.V. and K. Kadam, A comparative study on rigid and flexible pavement: A review. IOSR Journal of Mechanical and Civil Engineering (IOSR-JMCE), 2016. 13(3): p. 84-88.

[6] ehnood, A. and M.M. Gharehveran, Morphology, rheology, and physical properties of polymer-modified asphalt binders. European Polymer Journal, 2019. 112: p. 766-791.

[7] Luo, D., et al., The performance of asphalt mixtures modified with lignin fiber and glass fiber: A review. Construction and Building Materials, 2019. 209: p. 377-387.

[8] Hasan, M.R.M., et al., Review of sustainability, pretreatment, and engineering considerations of asphalt modifiers from the industrial solid wastes. Journal of Traffic and Transportation Engineering (English Edition), 2019. 6(3): p. 209-244.

[9] Wu, Y., et al., Geopolymer, green alkali activated cementitious material: Synthesis, applications and challenges. Construction and Building Materials, 2019. 224: p. 930-949.

[10] Malinowski, S., et al., Use of New Green Bitumen Modifier for Asphalt Mixtures Recycling. Materials, 2022. 15(17): p. 6070.

[11] de Azevedo, A.R., et al., Use of glass polishing waste in the development of ecological ceramic roof tiles by the geopolymerization process. International Journal of Applied Ceramic Technology, 2020. 17(6): p. 2649-2658.

[12] Aziz, A., et al., A state-of-the-art review of the structure and properties of laterite-based sustainable geopolymer cement. Environmental Science and Pollution Research, 2023: p. 1-18.

[13] Majdoubi, H., et al., Thermal, mechanical and microstructural properties of acidic geopolymer based on moroccan kaolinitic clay. Journal of Building Engineering, 2021. 35: p. 102078.

[14] Milad, A., et al., Utilisation of waste-based geopolymer in asphalt pavement modification and construction—A review. Sustainability, 2021. 13(6): p. 3330.

[15] Rosyidi, S.A.P., et al., Investigation of the chemical, strength, adhesion and morphological properties of fly ash based geopolymer-modified bitumen. Construction and Building Materials, 2020. 255: p. 119364.

[16] Tang, N., et al., Geopolymer as an additive of warm mix asphalt: Preparation and properties. Journal of cleaner production, 2018. 192: p. 906-915.

[17] Kong, D.L., J.G. Sanjayan, and K. Sagoe-Crentsil, Factors affecting the performance of metakaolin geopolymers exposed to elevated temperatures. Journal of Materials Science, 2008. 43: p. 824-831.

[18] Qaidi, S.M., et al., Sustainable utilization of red mud waste (bauxite residue) and slag for the production of geopolymer composites: A review. Case Studies in Construction Materials, 2022: p. e00994.

[19] Hossain, S.S., P. Roy, and C.-J. Bae, Utilization of waste rice husk ash for sustainable geopolymer: A review. Construction and Building Materials, 2021. 310: p. 125218.

[20] ASTM D5, Standard test method for penetration of bituminous materials. USA, ASTM International, 2013.

[21] ASTM D36, D36. Standard Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus). USA: American Society for Testing and Materials, 2009.

[22] AASHTO T315, Standard method of test for determining the rheological properties of asphalt binder using a dynamic shear rheometer (DSR). American Association of State Highway and Transportation Officials, 2012.

[23] Anderson, D.A., et al., Binder characterization and evaluation, volume 3: Physical characterization. Strategic Highway Research Program, National Research Council, Washington, DC, 1994

[24] Memon, A.M., et al., Modeling and optimization of mixing conditions for petroleum sludge modified bitumen using response surface methodology. Construction and Building Materials, 2020. 264: p. 120701.

[25] Wang, S., W. Huang, and A. Kang, Evaluation of aging characteristics of high-viscosity asphalt: Rheological properties, rutting resistance, temperature sensitivity, homogeneity, and chemical composition. Journal of Materials in Civil Engineering, 2021. 33(7): p. 04021149.