Potential of using organic additive produced with kaolin-clay in bituminous roadways

DOI : 10.36909/jer.17683

Deniz Arslan[*], Metin Gürü[**], M. Kürşat Çubuk[***], Meltem Çubuk[****], Farshad Karimzadeh Farshbafian[*****]

[*] Konya Technical University, Faculty of Engineering and Natural Sciences, Civil Engineering Department, 42075, Selçuklu/Konya, Turkey. e-mail: darslan@ktun.edu.tr Tel: +90-332-2051783 Fax: + 90-332-2410635
[**]Gazi University, Faculty of Engineering, Chemical Engineering Department, 06570, Maltepe/Ankara, Turkey. e-mail: mguru@gazi.edu.tr Tel: +90 312 582 3555 Fax: +90 312 230 8434
[***]Gazi University, Faculty of Engineering, Civil Engineering Department, 06570, Maltepe/Ankara, Turkey. e-mail: ckursat@gazi.edu.tr Tel: +90 312 582 3219 Fax: +90 312 230 8434
[****] Ministry of Transport and Infrastructure, 06500, Emek/Ankara, Turkey. e-mail: melcubuk@yahoo.com.tr Tel: +90 312 213 1000
[*****]Gazi University, Faculty of Engineering, Civil Engineering Department, 06570, Maltepe/Ankara, Turkey. e-mail: farshad.karimzadeh@gmail.com Tel: +90 312 582 3209 Fax: +90 312 230 8434
Corresponding author: Deniz Arslan Tel +90-332-223-1783; fax: + 90-332-2410635; darslan@ktun.edu.tr.

ABSTRACT

Roadway performance can be improved through utilizing modified bitumens and/or modified bituminous mixtures within the structure. Regarding this view, Kaolin-containing-Organic Additive Material (K-c-OAM) has been synthesized chemically in the study. K-c-OAM is a new additive material obtained in laboratory conditions with the reaction of kaolin, a kind of clay, and ethylene glycol. 50/70 penetration grade neat bitumen has been modified by K-c-OAM in concentrations ranging from 1 % to 4 %. The effects of K-c-OAM on both bitumen and bituminous mixture properties have been investigated by experiments including rotational viscosity, penetration, softening point, ductility, Nicholson stripping and Marshall tests. Marshall Stability values of the bituminous mixtures have been found to be increased at a level varying between 6.4 % and 9.5 % by K-c-OAM modified bitumens. In areas where hot climate is not dominant, K-c-OAM modified roadway pavements can said to provide better performance according to the laboratory findings.

Keywords: Kaolin; Kaolin-containing-Organic Additive Material; Marshall Stability; Modified bitumen; Stability/Flow

INTRODUCTION

Bitumen is a rheological material having colloidal properties. It is used as a binding agent in flexible roadway pavements. It coats aggregate particles, holds them together and provides flexibility to pavement structure. However, bitumen is highly influenced by environmental effects depending on its structural characteristics which can lead to undesired roadway pavement distresses. When bitumen or bituminous structures are exposed to a load, temperature has also great importance on deformations beside the magnitude and application period of that load. Moisture has negative effect on pavement strength as breaking adhesion at bitumen-aggregate interface. Oxygen and high temperature cause bitumen loose its properties over time which is known as ageing. Bitumen also plays a role on the fatigue life of pavement and its ductile property is effective against crack formations.

Having direct relationship with the strength of the roadway pavement, bitumen properties are trying to be improved by several additives. Clays draw attention among them. Clays with nano size (nano-clays) are used more often in order to make modification more effective. In studies carried out with nano-clay, higher rutting resistant parameters were obtained with nano-clay modified bitumens (Baqersad et al., 2019, Ashish and Singh, 2018).

Fatigue life was increased by adding nano-clay into bitumen (Akbari and Modarres, 2018). Montmorillonite, most common type of clay used to modifiy bitumen, was found to improve high temperature property but weaken low temperature property of bitumen (Jia et al., 2019). Similarly, viscosity of bitumen and its resistance to permanent deformation were increased by organo-functionalised montmorillonite nanoclay materials (Bagshaw et al., 2019). Unlike Jia et al. (2019), montmorillonite was said to improve low temperature performance of bitumen (Sedaghat et al., 2020). Nano-clay was found to enhance storage stability of SBS modified bitumen (Leng et al., 2019) and higher resistance against rut formation was observed in nanoclay modified mixtures compared to conventional mixtures (Carlesso et al., 2019). In a study where kaolin clay was added to the bitumen as a filler, higher viscosity, softening point and penetration index were obtained, but its effect on bituminous mixtures was not studied (Lebedev and Kozhukhova, 2018). Kaolin was used as aggregate replacement, rather than being an additive, which resulted to decrease density and void filled with bitumen ratio and increase stability of bituminous mixtures (Ingunza et al., 2013). Studies about effects of kaolin clay on bitumen and bituminous mixtures are not wide enough in literature and still need to be investigated. In this study, a new modifier, which we call organic additive material containing kaolin clay (K-c-OAM) has been synthesized chemically at laboratory conditions and used to modify a neat bitumen of 50/70 penetration grade with 'wet process'. In literature studies, clay was added as disperse. In that study, kaolin content was bonded to ethylene glycol chemically by means of H_2SO_4. An organo-compound (K-c-OAM) was prepared with kaolin and ethylene glycol. It is aimed to investigate the effects of K-c-OAM on bitumen properties by rotational viscosity, penetration, softening point, ductility tests. Penetration index values of neat and modified bitumen samples are also calculated and compared. The variations that K-c-OAM creates on the mechanical characteristics of bituminous mixtures are evaluated through Nicholson stripping and Marshall tests.

MATERIALS AND METHODS

Bitumen and aggregate

Bitumen with 50/70 penetration is frequently used in roadway pavements according to the climatic conditions of Turkey. Thus, 50/70 penetration grade neat bitumen has been used in the study. It has been supplied from Kırıkkale refinery of Turkey and its properties have been given in Table 1.

Table 1. Properties of 50/70 penetration grade neat bitumen

Property	Value
Penetration (25°C, 100 g, 5 s)	52 dmm (0,1 mm)
Softening point	50°C
Viscosity, @130°C	0.40 Pa.s
Viscosity, @140°C	0.24 Pa.s
Specific gravity, 25°C	1.04

Bituminous mixtures have been prepared with basalt aggregate for Marshall Design and Nicholson stripping tests. Aggregate has been supplied from Ankara/Kızılcahamam quarry. Specific gravity values for the aggregate portions and aggregate gradation used in Marshall samples have been shown in Tables 2 and 3, respectively.

Table 2. Specific gravity values for the aggregate fractions.

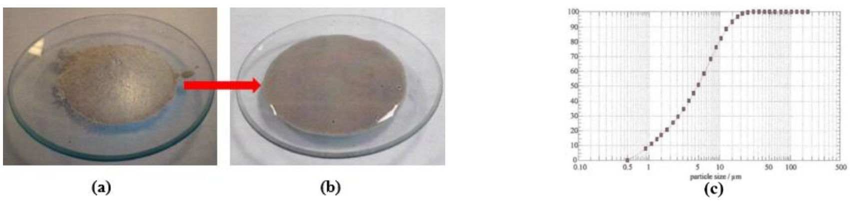
	Coarse Aggregate	Fine Aggregate	Filler
Bulk Specific Gravity	2.678	2.770	-
Apparent Specific Gravity	2.709	2.790	2.838

Table 3. Aggregate gradation used in Marshall Samples.

Sieve No.	3/4"	1/2"	3/8"	No.4	No.10	No.40	No.80	No.200
% Passing	100	91.5	80	47.5	31.5	15	10.5	7

Additive material

K-c-OAM was synthesized in laboratory with the reaction of ethylene glycol and kaolin at 120°C. Ethylene glycol was bought from Merck and its purity is ≥ 99 %. Its wholesale price ranges from 0.59 to 0.79 $/kg. Ethylene glycol and bitumen are compatible with each other in terms of their physical properties. Ethylene glycol expands performance temperature range of bitumen. Ethylene glycol is expected to increase flexibility and reduce brittleness of bitumen. Therefore, it has been preferred in the production of the additive. Kaolin (Figure 1a) is a kind of clay obtained from granite rocks. It is a kind of cheap material and has only energy consumption related to the separation of the rock into clay dimensions as a cost. Its retail price is 0.35 $/kg in Turkey. For one tonne of modified bitumen containing 3% K-c-OAM, the additive costs around $17 ($3,94 from kaolin, $12.94 from ethylene glycol). Particle size distribution of kaolin was given in Figure 1c. Sulfuric acid (H_2SO_4) was used as a catalyst in the reaction. Steps of the additive production are as follows: Ethylene glycol was put into the reactor and started to heat. Immediately after, 0.75 ml H_2SO_4 was added to glycol and mixed with a magnetic stirrer. At 80°C, kaolin was added to the reactor by degrees. Ethylene glycol-to-kaolin mass ratio was 5:3. Stirring was continued for 30 mins after the temperature reached to 120°C. At the end of the process; additive material, K-c-OAM (Figure 1b), was cooled to ambient temperature and kept hermetically into a jar.



(a) (b) (c)

Figure 1. Kaolin to K-c-OAM; **(a)** Kaolin, **(b)** K-c-OAM, **(c)** Particle size distribution of kaolin

Preparation of modified bitumens

Modified bitumens have been obtained by blending neat bitumen and K-c-OAM for 20 mins at 120°C by a mechanical mixer rotating with 1300 rpm. First, neat bitumen has been heated homogeneously in an oven at 120°C then the following K-c-OAM ratios (by weight of neat bitumen) have been added separately: 1%, 2%, 3%, 4% wt. Blending has been performed in an oil bath of 120°C in order to maintain mixing temperature during that process.

Methods

Brookfield DV III Rheometer with spindle no. 29 has been used to perform the rotational viscosity tests on the neat and K-c-OAM modified bitumen samples according to ASTM D-4402. Penetration, softening point and ductility measurements have been done in accordance with ASTM D-5, ASTM D-36 and ASTM D-113, respectively. EL46-4502 model ring and ball apparatus has been used in softening point tests. Ductility tests have been carried out at 15ºC. With the penetration and softening point results, Eq.1 has been used to calculate the penetration index values of the neat and modified bitumens.

$$\mathrm{PI} = \frac{1952 - 500 * \log(\mathrm{Pen}_{25°\mathrm{C}}) - 20 * \mathrm{SP}}{50 * \log(\mathrm{Pen}_{25°\mathrm{C}}) - \mathrm{SP} - 120} \quad (1)$$

where SP is the softening point of the bitumen sample (ºC) and $\mathrm{Pen}_{25ºC}$ is the penetration of the bitumen sample at 25ºC (dmm).

Marshall (ASTM D1559) and Nicholson Stripping (ASTM D1664) tests have been used to determine the effect of K-c-OAM modified bitumen on the mechanical properties of bituminous mixtures. Marshall Test samples have been manufactured at 145˚C with 1150 g basalt aggregate. Each sample has been compacted by 75 blows on both side with Marshall Compactor device (EL45-6600). Marshall design was made for wearing course. The adhesion force at the bitumen-aggregate interface has been evaluated with Nicholson stripping tests. The coarse basalt aggregate (6.3–9.5 mm) has been coated with neat and K-c-OAM modified bitumens separately at 110ºC. After immersing the loose mixtures in distilled water at 60ºC for 24 h, the stripping resistance of each mixture has been determined as the ratio of non-stripped aggregate surface to total aggregate surface.

RESULTS AND DISCUSSION

Viscosity test results

The effects of K-c-OAM on the fluidity of bitumen have been examined by viscosity tests. Rotational viscosity tests have been applied between 90-160ºC for this purpose. Figure 2 shows the variation of viscosity with respect to K-c-OAM concentration.

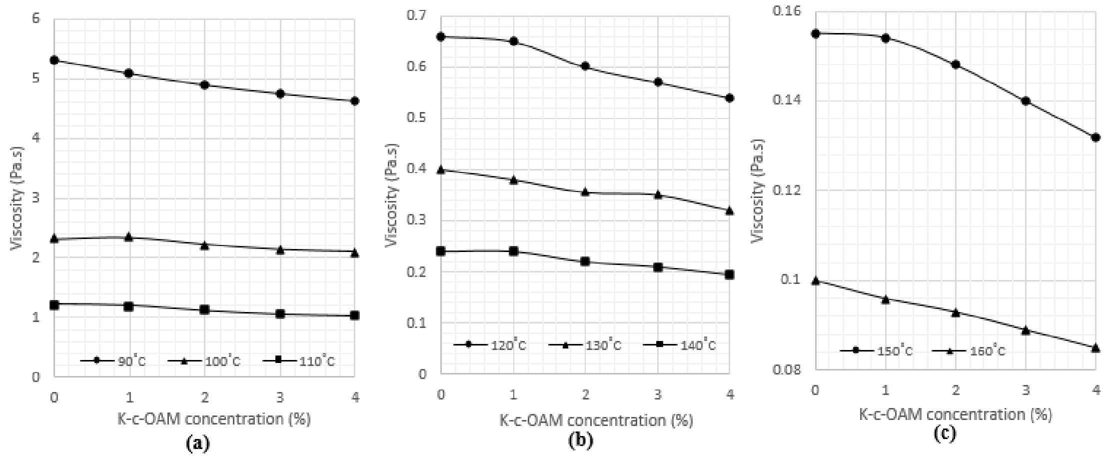


Figure 2. Variation of viscosity with respect to K-c-OAM concentration; **a.)** between 90˚C and 110˚C, **b.)** between 120˚C and 140˚C, **c.)** at 150˚C and 160˚C.

As seen in figures, viscosity of bitumen has been found to be decreased with the increasing content of K-c-OAM. Lower viscosity in K-c-OAM modified bitumens may allow plant temperature to be reduced during hot mix asphalt production, which leads to lower short term aging of bitumen, reduced emissions and reduced energy consumption since lower viscosity positively affects bitumen workability (Arslan et al., 2013, Arslan et al., 2012a, Arslan et al., 2012b). The temperature at which bitumen viscosity is obtained as 0.2 Pa.s is accepted as the optimum plant temperature. According to this approach, optimum plant temperature has been determined as 144.7ºC with neat bitumen, while reduced to 141.4ºC and 139.6ºC with 3 % and 4 % K-c-OAM modified bitumens, respectively which may offer the opportunity to provide somewhat above-mentioned benefits by K-c-OAM modified bitumen without claiming that K-c-OAM is a Warm Mix Additive.

Penetration, softening point and ductility test results

Penetration, softening point, ductility measurements and penetration index (PI) calculations are summarized in Table 4.

Table 4. Penetration, softening point, ductility and PI results of neat and K-c-OAM modified bitumens.

K-c-OAM concentration (%)	Penetration (dmm)	Softening point (ºC)	Ductility (cm)	PI
0	52	50	+100[a]	-1,116
1	54	50	+100[a]	-1,029
2	56	49	+100[a]	-1,120
3	59	48.5	+100[a]	-1,208
4	61	48	+100[a]	-1,262

[a] +100 means sample has not been broken in the test

Penetration is increased and softening point is decreased with K-c-OAM as expected (Table 4). Higher penetration and lower softening point caused PI to be decreased (except 1 % K-c-OAM modified bitumen), but not too much. The effect of K-c-OAM on the ductility could not be determined due to the test device limitations but all samples have been found to fulfill specification requirement by not breaking during the test.

Nicholson stripping test results

Nicholson stripping test is performed to evaluate the effect of K-c-OAM on the adhesion between bitumen and aggregate. According to the Nicholson stripping test results (Figure 3), adhesion force at the bitumen-aggregate interface is improved by using K-c-OAM modified bitumen. Stripping resistance have been found to be 95 % with neat bitumen, while 100 % with all K-c-OAM modified bitumens. In literature, such as K-c-OAM, organic-based calcium and manganese compounds, which cause a decrease in viscosity, increased stripping resistance, as well (Arslan et al., 2013, Arslan et al., 2012a, Arslan et al., 2014, Çubuk et al., 2013).

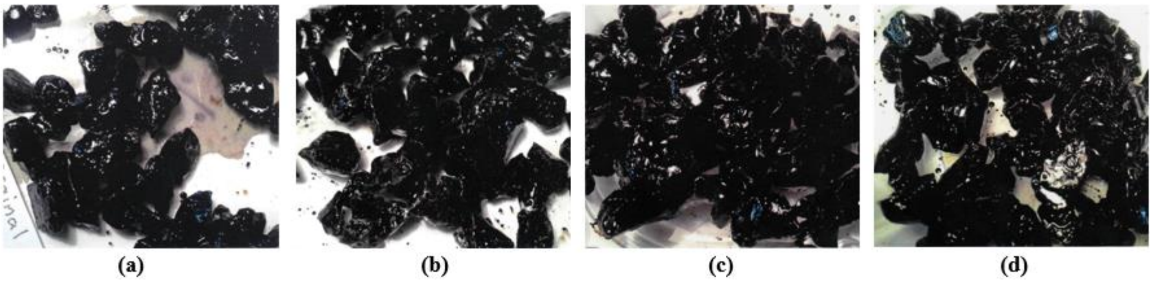


Figure 3. Nicholson stripping test results; **(a)** with neat bitumen, **(b)** with 1 % K-c-OAM modified bitumen, **(c)** with 2 % K-c-OAM modified bitumen, **(d)** with 3 % K-c-OAM modified bitumen.

Marshall test results

Stability values obtained from Marshall Tests are given in Figure 4. No significant change has been observed with neat and modified bitumens at low bitumen contents (4 % and 4.5 %). But, stability has been increased by K-c-OAM modified bitumens at higher bitumen contents (5 % and 5.5 %). Due to the viscosity decrease with K-c-OAM, more absorption will occur and thus, adhesion will be improved. The variation of air void ratios (Va) of samples depending on the bitumen content are shown in Figure 5. According to the Figure 5, optimum bitumen content, corresponding to Va of 4 %, for neat and modified bitumens are determined as 5.4 % for neat bitumen, 5.46 %, 5.48 % and 5.37 % for 1 %, 2% and 3 % K-c-OAM modified bitumens, respectively. So, using of original or modified bitumen did not produce a significant change in the optimum bitumen content for Marshall samples, whereas, stability at the optimum binder contents were predicted to be increased by 6.4-9.5 % with K-c-OAM modified bitumens (Figures 4-5). Since optimum bitumen rate will be used in the applications, K-c-OAM modified bitumens can be said to provide improvement on the stability of samples.

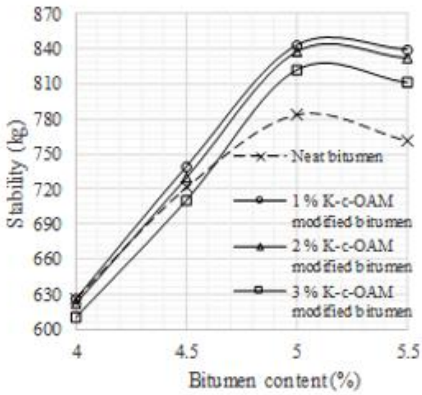


Fig. 4. Stability values of Marshall samples obtained by using neat and K-c-OAM modified bitumens.

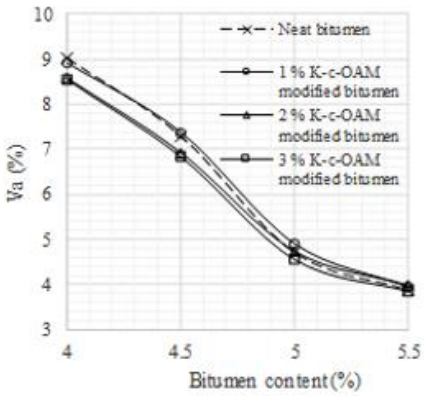


Fig. 5. Change in Va of Marshall samples depending on bitumen content.

As seen in Figure 6, flow trends of Marshall Samples appear to have irregularities. This is an issue that may arise from that test. Referring to Figure 7, where stability and flow parameters are evaluated together, it can be understood that the irregularities in the flow trends do not disturb the increase in stability obtained with modified bitumens. By adding flow effect to stability variable, improvements have also been achieved with K-c-OAM modified bitumens according to the criterion used as “stability / flow” which is evaluated as permanent deformation resistance parameter in previous studies (Morova et al., 2016). Higher parameter value is associated with higher resistance against permanent deformations like rutting, corrugation, etc. (Karakas et al., 2014).

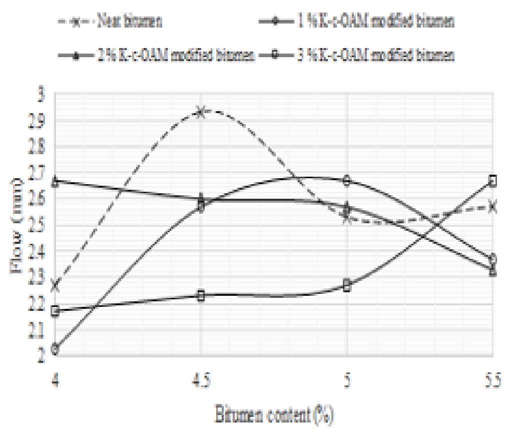


Fig. 6. Change in flow values of Marshall samples depending on bitumen content.

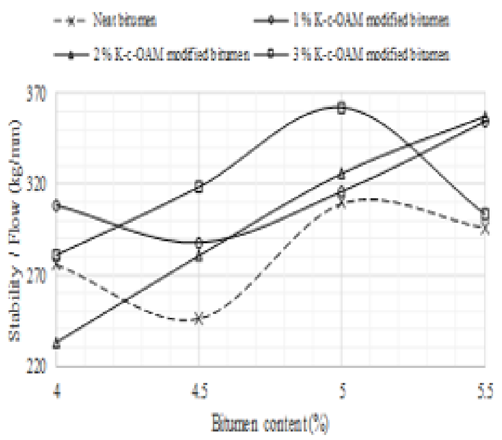


Fig. 7. Stability/Flow parameters of Marshall samples.

CONCLUSION

In this study, a new organic additive material containing kaolin, K-c-OAM, is synthesized chemically and is used to modify neat bitumen of 50/70 penetration grade. The differentiations on bitumen and bituminous mixture characteristics arisen from that modification process are summarized as follows;

- Viscosity of neat bitumen is found to be decreased with increasing content of K-c-OAM, which may allow plant temperature to be reduced (around 5ºC) during hot mix asphalt production. Thus, short-term aging of bitumen, emissions and energy consumption can be reduced somewhat with K-c-OAM modified bitumen.
- Penetration has been increased and softening point has been decreased by K-c-OAM modified bitumen. No adverse effect on the ductility is observed. According to the penetration and softening point results, PI is decreased but not too much.
- Nicholson stripping test has shown that adhesion force at the bitumen-aggregate interface is strengthened by K-c-OAM modified bitumen.

- No significant changes have been observed between neat and K-c-OAM modified bitumens in terms of optimum bitumen content (They are almost at the same level). However, K-c-OAM modified bitumens have been found to provide additional stability between 6.4-9.5 % in Marshall samples at the optimum bitumen content.
- Higher stability/flow values have been obtained in Marshall samples prepared with K-c-OAM modified bitumens.
- Lower modification parameters of K-c-OAM, 120ºC and 20 mins, are the other advantages of that additive material during modification process.

In areas where hot climate is not dominant, K-c-OAM modified roadway pavements can provide better performance due to improved mechanical characteristics especially on sections with high traffic volume, at bus stations and at-grade roadway intersections where acceleration and deceleration activities generally take place.

ABBREVIATIONS and SYMBOLS

H_2SO_4	Sulfuric acid
K-c-OAM	Kaolin-containing-Organic Additive Material
$Pen_{25ºC}$	Penetration of the bitumen sample at 25ºC
PI	Peneration index
SP	Softening point
Va	Air void ratio

REFERENCES

Akbari, A., Modarres, A. 2018. Evaluating the effect of nano-clay and nano-alumina on the fatigue response of bitumen using strain and time sweep tests. International Journal of Fatigue, 114: 311-322. https://doi.org/10.1016/j.ijfatigue.2018.06.007

Arslan, D., Gürü, M., Çubuk, M.K. 2012a. Performance assessment of organic-based synthetic calcium and boric acid modified bitumens. Fuel, 102: 766-772. https://doi.org/10.1016/j.fuel.2012.06.038

Arslan, D., Gürü, M., Çubuk, M.K. 2012b. Bitüm ve bitümlü karışımların performans özelliklerinin organik esaslı çinkofosfat bileşiği ile geliştirilmesi. Journal of the Faculty of Engineering and Architecture of Gazi University, 27: 459-466.

Arslan, D., Gürü, M., Çubuk, M.K. 2013. Improvement of hot mix asphalt performance in cold regions by organic-based synthetic compounds. Cold Regions Science and Technology, 85: 250-255. https://doi.org/10.1016/j.coldregions.2012.09.014

Arslan D, Gürü M, Çubuk M.K. 2014. Preventing of rutting and crackings in the bituminous mixtures by monoethylene and diethylene glycol based synthetic polyboron compounds. Construction and Building Materials, 50: 102-107. https://doi.org/10.1016/j.conbuildmat.2013.09.039

Ashish, P.K., Singh, D. 2018. Development of empirical model for predicting G*/Sinδ and viscosity value for nanoclay and Carbon Nano Tube modified asphalt binder. Construction and Building Materials, 165: 363-371. https://doi.org/10.1016/j.conbuildmat.2018.01.021

ASTM D5 2013. Standard Test Method for Penetration of Bituminous Materials. 10.1520/D0005-06E01

ASTM D36 2010. Standard Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus). 10.1520/D0036-06

ASTM D113 2018. Standard Test Method for Ductility of Asphalt Materials. 10.1520/D0113-17

ASTM D1559. Standard Test Method for Resistance to Plastic Flow of Bituminous Mixtures Using Marshall Apparatus.

ASTM D1664. Test Method for Coating and Stripping of Bitumen-Aggregate Mixtures.

ASTM D4402 2022. Standard Test Method for Viscosity Determination of Asphalt at Elevated Temperatures Using a Rotational Viscometer. 10.1520/D4402_D4402M-15R22

Bagshaw, S.A., Kemmitt, T., Waterland, M., Brooke, S. 2019. Effect of blending conditions on nano-clay bitumen nanocomposite properties. Road Materials and Pavement Design, 20:1735-1756. https://doi.org/10.1080/14680629.2018.1468802

Baqersad, M., Ali, H., Haddadi, F., Khakpour, I. 2019. Short- and long-term rheological and chemical characteristics of nanomodified asphalt binder. Petroleum Science and Technology, 37: 1788-1799. https://doi.org/10.1080/10916466.2019.1602635

Carlesso, G.C., Trichês, G., Staub de Melo, J.V., Marcon, M.F., Thives, L.P., Carolina da Luz,,L. 2019. Evaluation of Rheological Behavior, Resistance to Permanent Deformation, and Resistance to Fatigue of Asphalt Mixtures Modified with Nanoclay and SBS Polymer. Applied Sciences-Basel, 9: 2697. https://doi.org/10.3390/app9132697

Çubuk M, Gürü M, Çubuk M.K., Arslan D. 2013. Improvement of properties of bitumen by organic-based magnesium additive. Journal of the Faculty of Engineering and Architecture of Gazi University 28: 257-264.

Ingunza, MdPD., Junior, OFdS., Costa, CG. 2013. Recycling of kaolin processing waste as aggregate in asphalt concrete. Advanced Materials Research, 717: 21-26. https://doi.org/10.4028/www.scientific.net/AMR.717.21

Jia, M., Zhang, Z., Wei, L., Wu, X., Cui, X., Zhang, H., Lv, W., Zhang, Q. 2019. Study on properties and mechanism of organic montmorillonite modified bitumens: View from the selection of organic reagents. Construction and Building Materials, 217: 331-342. https://doi.org/10.1016/j.conbuildmat.2019.05.074

Karakas, A.S., Sayın, B., Kuloğlu, N. 2014. The changes in the mechanical properties of neat and SBS-modified HMA pavements due to traffic loads and environmental effects over a one-year period. Construction and Building Materials, 71: 406-415. https://doi.org/10.1016/j.conbuildmat.2014.08.060

Lebedev, M.S., Kozhukhova, N.I. 2018. Rheological characteristics of bitumen mastic depending on composition and filler dispersity. J. Phys.: Conf. Ser. 1045, 012026.

Leng, Z., Tan, Z., Yu, H., Guo, J. 2019. Improvement of storage stability of SBS-modified asphalt with nanoclay using a new mixing method. Road Materials and Pavement Design, 20 (7), 1601-1614. https://doi.org/10.1080/14680629.2018.1465842

Morova, N., Serin, S., Terzi, S., Saltan, M., Kucukcapraz, D.O., Karahancer, S.S., Eriskin, E. 2016. Utility of polyparaphenylene terephtalamide fiber in hot mix asphalt as a fiber. Construction and Building Materials, 107: 87-94. https://doi.org/10.1016/j.conbuildmat.2015.12.193

Sedaghat, B., Taherrian, R., Hosseini, S.A., Mousavi, S.M. 2020. Rheological properties of bitumen containing nanoclay and organic warm-mix asphalt additives. Construction and Building Materials, 243: 118092. https://doi.org/10.1016/j.conbuildmat.2020.118092