

The Microstructural and Mechanical Characterization of Organo-Clay-Modified Bitumen, Calcareous Aggregate, and Organo-Clay Blends

A. Gürses, T. B. Barın, Ç. Doğar

I. INTRODUCTION

Abstract—Bitumen has been widely used as the binder of aggregate in road pavement due to its good viscoelastic properties, as a viscous organic mixture with various chemical compositions. Bitumen is a liquid at high temperature and it becomes brittle at low temperatures, and this temperature-sensitivity can cause the rutting and cracking of the pavement and limit its application. Therefore, the properties of existing asphalt materials need to be enhanced. The pavement with polymer modified bitumen exhibits greater resistance to rutting and thermal cracking, decreased fatigue damage, as well as stripping and temperature susceptibility; however, they are expensive and their applications have disadvantages. Bituminous mixtures are composed of very irregular aggregates bound together with hydrocarbon-based asphalt, with a low volume fraction of voids dispersed within the matrix. Montmorillonite (MMT) is a layered silicate with low cost and abundance, which consists of layers of tetrahedral silicate and octahedral hydroxide sheets. Recently, the layered silicates have been widely used for the modification of polymers, as well as in many different fields. However, there are not too much studies related with the preparation of the modified asphalt with MMT, currently. In this study, organo-clay-modified bitumen, and calcareous aggregate and organo-clay blends were prepared by hot blending method with OMMT, which has been synthesized using a cationic surfactant (Cetyltrimethylammonium bromide, CTAB) and long chain hydrocarbon, and MMT. When the exchangeable cations in the interlayer region of pristine MMT were exchanged with hydrocarbon attached surfactant ions, the MMT becomes organophilic and more compatible with bitumen. The effects of the super hydrophobic OMMT onto the micro structural and mechanic properties (Marshall Stability and volumetric parameters) of the prepared blends were investigated. Stability and volumetric parameters of the blends prepared were measured using Marshall Test. Also, in order to investigate the morphological and micro structural properties of the organo-clay-modified bitumen and calcareous aggregate and organo-clay blends, their SEM and HRTEM images were taken. It was observed that the stability and volumetric parameters of the prepared mixtures improved significantly compared to the conventional hot mixes and even the stone matrix mixture. A micro structural analysis based on SEM images indicates that the organo-clay platelets dispersed in the bitumen have a dominant role in the increase of effectiveness of bitumen - aggregate interactions.

Keywords—Hot mix asphalt, stone matrix asphalt, organo clay, Marshall Test, calcareous aggregate, modified bitumen.

ASPHALT has been widely used as the binder of aggregate in pavements due to its good viscoelastic properties. Bitumen which is liquid at high temperatures starts to become brittle at low temperatures [1], [2]. Moisture in bituminous mixtures could cause to a reduction of effective adhesive and cohesive interactions at the binder- aggregate interface and within binder or binder/filler mastic. Therefore, the damages resulting from the loss of strength, stiffness and durability can be evaluated by considering the moisture content of bituminous mixtures. The various approaches to improve adhesion and reduce moisture sensitivity in asphalt mixtures have been developed. One of them is based on the fact that binder-aggregate interfacial energy may be reduced by adsorption of oppositely charged surfactant ions on the surface of aggregates having negative surface charge [3]. Stone mastic asphalt (SMA), which can exhibit a high resistance to permanent deformation is prepared by high coarse aggregate content to form a stable network or stone skeleton structure. The voids in the network structure are filled with a gum of bitumen and filler, which includes fiber. The fibers are used to control viscosity of bitumen and prevent drainage of binder under load. Recently, the layered silicates have been widely used especially for the modification of polymers and for the preparation of polymer-clay nanocomposites [4]-[6]. Layered silicates are the low-cost and widely available minerals which are formed of tetrahedral silicate and octahedral aluminum hydroxide layers [7]-[9]. The types of layered silicate such as MMT, rectorite (REC), Vermiculite (VMT) and Kaolinite are widely known. The intercalation of polymer chains into the interlayer region of clay can be performed using various processes such as the melt intercalation and the solution intercalation. Such a modification can lead to the significant improvements in the thermal, mechanical and barrier properties of polymers [10]-[13]. The promising new alternatives for the improvement of engineering properties (stiffness and strength) of mixtures use various additives such as polymer and organo-clay. The modification of asphalt by polymers may produce a new material (polymer-modified asphalt - PMA), which sometimes has very different mechanical properties from the conventional asphalt. Styrene-butadiene-styrene copolymer (SBS), styrene butadiene rubber (SBR), rubber, ethylene vinyl acetate (EVA), and polyethylene may be generally listed as the polymers used for modification of asphalt [14], [7], [15]. Although only a few studies into asphalt modification with MMT are available,

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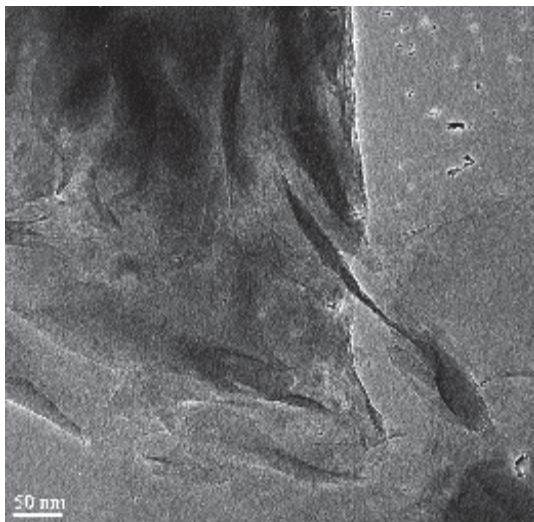
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there is no study on the use of organo-clay as bifunctional for hot mix asphalt (creating spatial network effect and preventing the drainage of binder), currently. This study aims the microstructural and mechanic characterization of organo-clay-modified bitumen, and calcareous aggregate and organo-clay blends (the stabilized HMAs). Also, the water intake levels of the prepared blends (i.e., the moisture content (%)) of the specimens which have been dried superficially) were used to evaluate relatively, the susceptibility of the blends toward moisture.

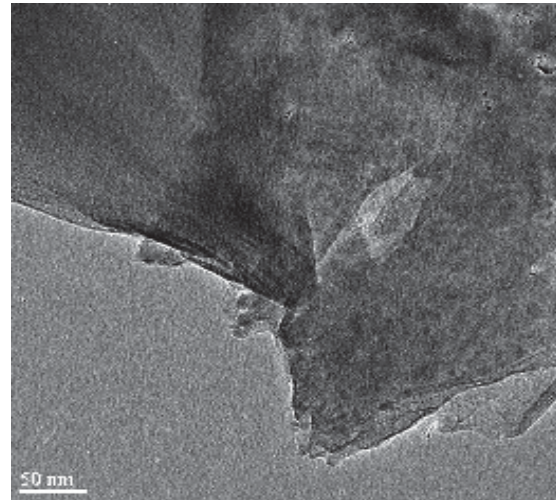
II. MATERIALS AND METHODS

A. The Preparation and Characterization of Organo-Clay

In this study, CTAB, a cationic surfactant, was used to synthesize extraordinary organophilic clay and to obtain the dispersion in water of long chain hydrocarbon agent to produce organic cations having longer hydrophobic tail [16]. Na-MMT, which is commercial and widespread clay, was supplied from the Çankırı region in Turkey. The cation exchange capacity (CEC) of the clay used was measured as 147.9 meq/100 g by Methylene blue method [17]. The chemical composition of MMT, which has been determined by X-ray fluorescence spectrometry technique, was given in Table I. The some typically properties of commercial long chain hydrocarbon and bitumen used in this study were shown in Tables II and III, respectively. Organo-clay (OMM) has been prepared by the solution-intercalation method with the combination of CTAB and long chain hydrocarbon, using Na-MMT (With 240 mg / L CTAB concentration and long chain hydrocarbon ratio of 0.3 g/1.0 g clay). The micro-structures of raw Na-MMT and the OMM have been studied by using the images taken from High Resolution Transmission Electron Microscope (HRTEM) (JEOL 2100, LaB6 filament) at 200 kV (Fig. 1).



(a)



(b)

Fig. 1 The HRTEM images of raw Na-MMT (a) and OMM (b)

Fig. 1 shows that the organo-clay platelets having a high interaction potential with the other components were formed. Thus, it can be suggested that the highly hydrophobic platelets will have the surface characteristics highly compatible to bitumen and aggregate. When comparing of the both images by considering the dispersed clay plates, it can be concluded that organo-clay has possessed a higher surface area. It is extremely important in terms of the adhesive interactions.

Also, the SEM images which belong to the control mix containing 10 wt. % organo-clay, the stabilized HMA having optimal mechanical values and a conventional mix without organo-clay, in the same gradation were taken by using SEM (FEI-INSPECT S50 model) at 30 kV (Fig. 4).

TABLE I
THE CHEMICAL COMPOSITION OF RAW CLAY

SiO ₂	59.32
Al ₂ O ₃	17.19
CaO	2.21
MgO	3.63
Fe ₂ O ₃	5.95
K ₂ O	0.97
Na ₂ O	1.68
TiO ₂	0.74
SO ₃	0.51
Other	7.81

TABLE II
PHYSICAL AND CHEMICAL PROPERTIES OF LONG CHAIN
HYDROCARBON USED IN THIS STUDY

Density (15 °C), kg/m ³	990.7
Calorific value MJ/kg	42.74
Flash point °C	105.8
Water by distillation, wt. %	0.1
C	83.4
H	11.9
N	0.8
S	1.5
Ash	0.03

TABLE III
PHYSICAL PROPERTIES OF BITUMEN USED IN THIS STUDY

Properties	Standard	Asphalt type B 50 – 70
Specific gravity at 25 °C (g/cm ³)	ASTM D70	1.041
Penetration at 25 °C (0.1 mm 100g 5 s)	ASTM D5	70
Softening point (°C)	ASTM D36	51

B. Preparation of Marshall Specimens

There are three principal bituminous mix design methods, such as *Marshall Method*, *Hveem Method* and *Super pave Method* in general use. Marshall-mix design, which is the widely used method, is applied to a cylindrical specimen of the bituminous mix and the sample is monitored until failure, as specified in the ASTM D1559 standard. In this work, the calcareous aggregate and organo-clay blends (the stabilized HMAs) are designed using the Marshall Method and then their stabilities with the volumetric properties of the prepared specimens have been measured. This test procedure that is used in designing and evaluating bituminous paving mixes has two major features (density-voids analysis and stability-flow test). Strength is measured in terms of the *Marshall's Stability* of the mix, which is defined as the maximum load carried by a compacted specimen at 60 °C. Flexibility is determined using the flow value which is associated with the change in the diameter of sample in the application direction of load between initial loading and maximum loading and corresponds to the plastic flow (deformation) during the failure of specimen. The density-voids analysis is also done using the volumetric properties of the mix.

The mix design mainly refers to determining the binder and aggregates volumes, which is necessary to produce a mixture having certain features. The bulk specific gravity (D_p), the percentage air voids (VA), the percentage void in the mineral aggregate (VMA), and the percentage voids filled with bitumen (VFB) may be defined as the main volumetric properties for bituminous mixtures. Air voids percent (VA) that is defined as a percent of the bulk volume of the compacted mixture is extremely important in terms of the evaluating of stability, durability and permeability parameters.

The total volume of voids including the air voids and the volume of non-absorbed bitumen in the aggregate mix is defined as voids in VMA. VMA corresponds to the volume of intergranular voids between the aggregate particles, and is expressed as a percentage of the total volume of the mix. The mixtures having low VMA value exhibit a higher sensitivity to the content of binder. Also, the smaller values than 17 % mean that there are not enough voids within the mixture for adding enough binder to cover the surface of aggregate particles [18].

The VFB (voids filled with bitumen) corresponding to the voids in the mineral-aggregate framework filled with bitumen binder represents the content of effective bitumen (in volume). VFB, which can be defined also as the percentage in volume of the VMA filled with bitumen is inversely proportional with the percentage of air voids. Thus, the decrease in air voids means to an increase in VFB. The decrease of VFB also indicates a decrease of effective bitumen film thickness

between aggregates. A thin bitumen film can lead to an increased low temperature cracking behavior and decreased durability, because bitumen is responsible for the filling and healing effects to improve the flexibility of the mixture [18].

C. Gradation of Aggregates

Gradation of aggregates is one of the most important factors for the design of HMA mixtures. The calcareous gravel aggregates used for the design of the mix in this study were supplied from Aşkale region in Erzurum-Turkey. To set the organo-clay ratio for each design mix, firstly the filler has been withdrawn and then the amount of the fine aggregate in the fractions of the gradation is reduced in the ratio corresponding to the increased organo-clay. Tables IV and V show the aggregate gradation and their specific gravities, respectively.

TABLE IV
THE AGGREGATE GRADATION FOR THE MIX DESIGNED AT THIS STUDY

inch	mm	% 15 (3/4"-1/2")	% 37.5 (1/2"-No.4)	% 47.5* (No.4-No.200)	Average (%)
3/4	19.0	100.0	100.0	100.0	100.0
1/2	12.5	52.4	100.0	100.0	92.9
3/8	9.5	6.2	87.9	100.0	81.4
No.4	4.75	0.7	15.8	100.0	53.5
No.10*	2.00	0.5	1.0	72.0	34.7
No.40*	0.42	0.4	0.8	34.2	16.6
No.80*	0.18	0.3	0.8	22.4	11.0
No.200*	0.075	0.3	0.7	11.0	5.5

* These fractions were used to set the organo-clay content of each design mix.

TABLE V
BULK AND APPARENT SPECIFIC GRAVITY VALUES OF THE AGGREGATE

Grain-size fraction	Bulk specific gravity (g/cm ³)	Apparent specific gravity (g/cm ³)
Coarse aggregate	2,686	2,716
Fine aggregate	2,690	2,723
Filler aggregate	2,735	-
Organo-clay	1,952*	-
Ash		0.03

* It was measured by He pycnometry technique.

Marshall Stability tests were conducted on various samples of 100 mm diameter and 63.5 mm height by applying 75 blows on each face according to the standard procedure of ASTM D1559. Bituminous mixes are prepared by mixing the graded aggregates with 50/70 penetration grade bitumen (Table III) and organo-clay in various ratios. Bitumen ratio was kept constant as 6.0 % wt., except for the experiments, in which the effect of bitumen ratio was examined. Each test was performed at least in triplicate.

The compacted specimens with the proposed design mix gradation have been prepared at the various organo-clay ratios (12.5-20.0 % wt.) and a constant bitumen ratio. The organo-clay content of the prepared mixes has been adjusted by decreasing the fractions in the range of 2.0-0.075mm in percentage by weight of the total mix. As soon as the freshly compacted specimens have cooled to room temperature, the bulk specific gravity of each test specimen was determined.

The same procedure was repeated for optimal organo-clay ratio at the various bitumen ratios (4.25-6.25 % wt.). The stability and flow value of each test specimen was then determined. After the completion of the stability and flow test; specific gravity and voids analysis was carried out for each test specimen to determine the percentage air voids in mineral aggregate and the percentage of air voids in the compacted mix and voids filled with bitumen. Using the average of the values measured for the bulk specific gravity, the stability and flow, with the parameters, such as VA, VMA and VFB, the Marshall curves were obtained by plotting separately against the organo-clay and bitumen ratio, as shown in Figs. 2 and 3. The optimum bitumen content (OBC) for the HMAs, which is prepared to determine the effect of the organo-clay ratio, has been adjusted as 6.0% by weight. The HMA mixture with 10.0 wt. % organo-clay content (without filler) has been considered as the control mixture for all the subsequent tests.

D. The Evaluating of the Moisture Susceptibility in terms of Moisture Content

It is well known that presence of moisture in a bituminous mix is a critical factor, which leads to premature failure of the flexible pavement and to the loss of adhesion of aggregates with bitumen. In order to examine the effect of the organo-clay on the moisture content of the Marshall specimens; the specimens of 100 mm diameter and 63.5 mm height are prepared and conditioned by keeping in water bath maintained at 60 °C for 45 minutes prior to measuring. The moisture content, as percentage, was calculated as based on the difference of weights of the superficially dried specimen with the conditioned specimen in water of the same mix. A lower value implies lower moisture susceptibility or lower moisture adsorbing capacity (higher moisture damage resistance). Marshall Quotient (MQ), which is known also as the rigidity

ratio, is the ratio of stability of the mixture to its flow value. MQ values of these specimens were also calculated.

TABLE VI
MQ VALUES CALCULATED IN THE VARIOUS ORGANO-CLAY RATIOS AND CORRESPONDING MOISTURE CONTENTS

Organo clay ratio (%)	Moisture content (%)	MQ
10.0	0.04	1.13
12.5	0.01	2.20
15.0	0.07	3.23
17.5	0.04	5.28
20.0	0.04	4.04

TABLE VII
MQ VALUES CALCULATED IN THE VARIOUS BITUMEN RATIOS AND CORRESPONDING MOISTURE CONTENTS

Bitumen ratio (%)	Moisture content (%)	MQ
4.25	0.20	3.47
4.50	0.13	4.01
4.75	0.10	4.23
5.00	0.08	4.54
5.75	0.05	6.93
6.25	0.15	7.03

The Marshall Quotient values calculated for the specimens prepared with various organo-clay contents and bitumen percentages have been given together with their moisture contents in Tables VI and VII.

III. RESULTS AND DISCUSSION

The test results of volumetric and mechanical properties for the hydrocarbon doped organo-clay stabilized mixtures were presented in the following sections.

A. Marshall Stability and Flow Value

Marshall curves for the specimens with various organo-clay ratios and various bitumen ratios were given in Figs. 2 and 3.

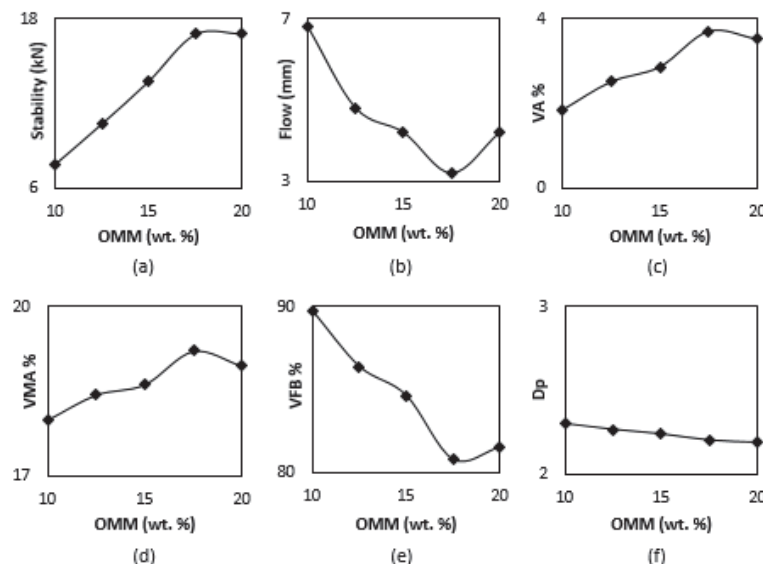


Fig. 2 The Marshall curves for various organo-clay ratios

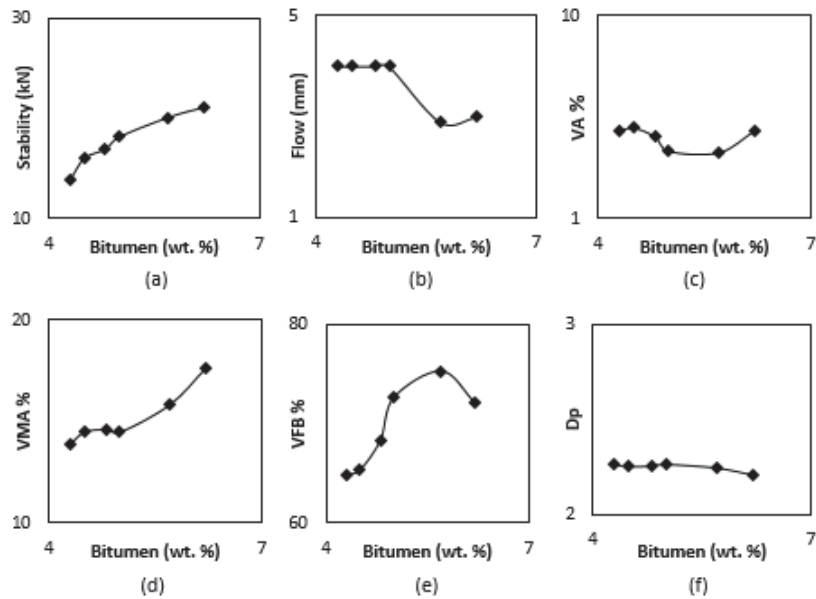


Fig. 3 The Marshall curves for various bitumen ratios

Fig. 2 indicates that the stability values of the OMM-stabilized mixtures increase initially reach a maximum value and then remain constant with the increase of the OMM ratio. It can be concluded that the organo-clay platelets were highly compatible with the surface characteristics of bitumen and aggregate. It may also imply providing a large surface area, which will promote the adhesion interactions between bitumen and aggregate. This is compliant with the fact that the mixture containing organo-clay shows higher performance according to the control mixture. Bituminous mixture is an inconsistent, non-uniform, multi-phased composite material consisting of aggregates and sticky bitumen. Therefore, excessive organo-clay may not disperse uniformly, and even coagulate forming weak points inside the mixture. In order to make a comparative evaluation about the effectiveness of the adhesive interactions between aggregate, organo-clay and bitumen with the formation of different network arrangements in microscopic scale; the SEM images of the three different specimens are given in Fig. 4. The specimens consisted of the conventional mix (without the organo-clay), the control mix containing organo-clay of 10.0 wt. %, and the stabilized HMA which has optimal mechanical values and the same gradation with others. These images reveal the presence of more effective adhesion interactions between aggregate and organo-clay modified bitumen which could provide the formation of a different framework than that of other specimens, in the case of the mix containing 17.5 wt. % of organo-clay. Comparing the different OMM-stabilized mixtures, it is evident that the mix containing 17.5 wt. % of organo-clay has the highest stability (16.91 kN), indicating their higher rutting resistance and better performance than other mixtures. The percentage increase in stability with respect to the control mixture is about 200 for this mixture. This result could be attributed to the effective adhesion behavior and spatial networking effect of hydrocarbon doped organo-clay platelets, in the case of the

stabilized mixtures. It is known that the spatial networking effect was regarded as the primary factors contributing to fiber's reinforcement [19]-[21].

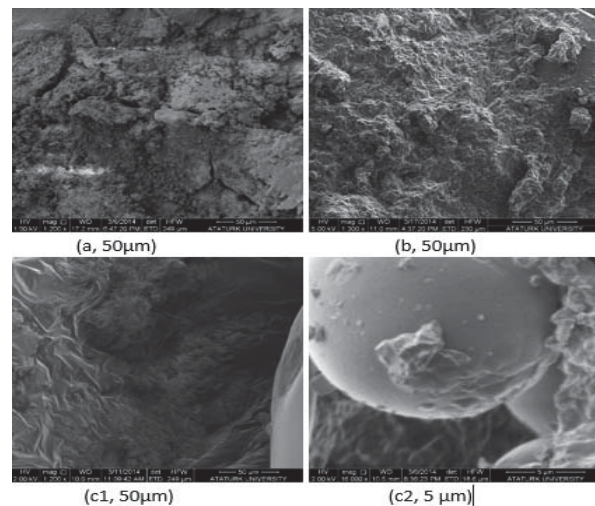


Fig. 4 SEM images for the three different specimen: (a) the conventional mix (without the organo-clay), (b) the control mix (containing 10.0 wt. % of organo-clay), and (c1 and c2) the OMM-stabilized HMA (having the optimal mechanical values)

This trend could be explained as follows: fiber performs as a “bridge” when cracking of bitumen mixture appears and thus resists the propagation of cracking development, which is known as the bridging cracking effect [2]. In addition, due to the effective interactions between bitumen and organo-clay platelets, organo-clay improves the viscosity and stiffness of bitumen, as similar to the effect of the fibers [22]. From Fig. 3, it can be seen that the stability values of the OMM-stabilized mixtures increases with the increasing bitumen ratio. This is

an expected result of possible effective adhesion interactions between super hydrophobic organo-clay platelets and bitumen. Accordingly, it can be suggested that the presence of hydrocarbon doped organo-clay in the HMA mixtures lead to the improved stability and flow values.

It can be seen from Fig. 2 that the bulk specific gravity values of the stabilized mixtures decrease with the increasing content of organo-clay. This decreasing trend was similar to the results obtained in the SMA mixture [23]. This result would be attributed to the much lower specific gravity of organo-clay than that of aggregates. Meanwhile, the elastic behavior of mixture increases with increase in organo-clay content, due to the probable exfoliated dispersion in the bituminous mixture of the hydrocarbon doped organo-clay platelets and so the reduction of bitumen-aggregate interfacial energy [24].

It is known that the lower air void may lead to increased plastic flow and thus bitumen bleeding. On the other hand, excessive air voids and hence an insufficient coating of the binder onto the aggregates may cause to cracking [18]. Fig. 2 (c) show that the air voids increase after adding organo-clay into bituminous mixtures. This may be due to the networking effect of the organo-clay within the mix (lower D_p correlates to higher air voids). The mixtures with higher organo-clay content have the highest air voids than the control mix. However, the air voids of the organo-clay reinforced specimens are in the specification range of 3 % to 5 %, too. The VMA values of HMA mixtures increase with increased organo-clay content. Whereas, their VFB values initially increase and then decrease (Figs. 2 (d) and (e)).

B. Optimization of Design Variables

The optimization of design parameters was carried out considering the different ranges of variables, such as organo-clay and bitumen ratio with Response Surface Methodology (RSM), a statistical optimization, by using MINITAB 15 software, to minimize the flow and water absorption to maximize stability. The optimization curves plotted for both design variables were shown in Fig. 5.

The optimum organo-clay ratios (% wt.) were determined to be 17.17, 10.00 and 19.17, respectively, for flow behavior, water absorption and stability. However, the optimum bitumen ratios (% wt.) for the same functions were designated to be 6.53, 6.79 and 6.27, respectively.

IV. CONCLUSION

The outstanding results of this study can be summarized as following:

- Unlike the conventional procedures used for the synthesis of organo-clay, the super hydrophobic organo-clay (OMM) was synthesized by the solution-intercalation method using Na-MMT and the long chain hydrocarbon-attached Cetyltrimethylammonium ions.
- The mechanical measurement results of the mixtures imply that the surface characteristics of organo-clay plates became highly compatible to the surface characteristics of

bitumen and aggregate, creating a large surface area extremely convenient for the adhesion interactions.

- It was found that the HMAs reinforced-OMM exhibited significant improvements in the stability values and volumetric parameters with the extremely low moisture contents, compared to the conventional hot mix asphalt (HMA) and even to the stone matrix asphalt (SMA).
- When the hydrocarbon doped organo-clay is added into the mix as only slightly excess as the filler ratio used for conventional hot mix asphalts (HMAs); it can act as a bifunctional structural component, which could prevent the drainage of binder and create spatial networking effect.
- The optimum values (% wt.) of organo-clay and bitumen ratios for flow, water absorption and stability were determined to be 17.17, 10.00 and 19.17 and 6.53, 6.79 and 6.27, respectively.

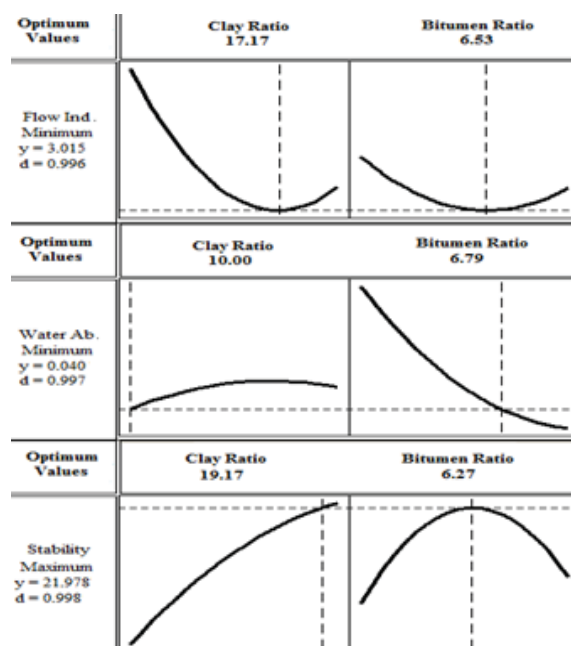


Fig. 5 Functional surface analysis results and optimization curves for the two design variables, organo-clay ratio and bitumen ratio

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