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Zeta Potential of Aggregate and Dynamic Modulus of HMA Estimation Using Aggregate Silica Content

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Abstract

The mineralogical composition of an aggregate influences its adhesion with bitumen and therefore its dynamic modulus. However, few studies have been conducted on this aspect. One of the most used properties to describe the impact of aggregate on the adhesiveness phenomena is the zeta potential. In this study, the first mineralogical and chemical properties were considered through the percentage of silica in the rock source of aggregates and the electric aggregate particles charge zeta. Dynamic modulus values used for regression process are determined from complex modulus test on nine asphalt concretes mix designed with aggregate types (basalt of Diack, quartzite of Bakel and Limestone of Bandia). The results showed that aggregate with high percentage of silica have higher zeta potential than aggregate with low percentage of silica. The development of a zeta potential predictive model showed a strong sensitivity to silica. The results of the complex modulus tests showed that Hot Mixture Asphalt (HMA) mixed with aggregate containing high silica contents gave better results than those mixed with aggregates containing low percentage of silica. The dynamic modulus predictive models of HMA developed shows that it is the properties of bitumen that influence more. However, the effect of silica although low, is very marked at low temperatures and high frequencies.

Keywords

Basalt of Diack, Quartzite of Bakel, Limestone of Bandia, Complex Modulus Test, Binder-Aggregate Adhesiveness

1. Introduction

In the search for high performance in the study of bituminous materials, zeta potential brings significant information. However, it is more focused on the study of bituminous binders, bituminous mastics and adhesiveness. One of the main parameters representing aggregates particles is the zeta potential. It expresses the load that has a particle because of the ion cloud surrounding it when it is in suspension. Several studies have been done on the impact of the zeta potential on the properties of bituminous materials. For example, studies carried out by Korean Society of Transportation [1] on stripping of asphalt pavements and antistripping addities showed that aggregates which had relatively higher surface potential in water and/or which imparted relatively higher pH to the contacting water were more susceptible to stripping. The zeta potential can be positive or negative, it will depend on the stability of the suspended particles [2] [3] [4]. A value of 25 mV (positive or negative) can be taken as arbitrary value that separates the low-load surfaces to highly charged surfaces Delgado and Robatti [2] [3] were among the first to use electrokinetic property of aggregate particles to explain the stiffening effect of filler on the asphalt mastic and to develop a predictive model. Faheem and Bahia (2010) introduced a conceptual model for the filler stiffening effect of mastic. They postulated that the filler stiffening effect varies depending on the filler mineralogy and the concentration in the mastic. Richardson and Clifford [5] reported that certain types of fillers such as silica, limestone dust, and Portland cement adsorb relatively thicker film of asphalt. The purpose of all these studies cited above is to better understand the mechanisms of binder-aggregate adhesivity in order to formulate HMAs with better performance. This article is interested in the performance of the stiffness translated by the dynamic modulus. In this paper, the objective is to measure the impact of the nature of aggregate in the zeta potential test results. The aggregates used are differentiated by their percentage of silica (SiO_2), and secondly to measure this impact on the measurement and prediction of the dynamic modulus of HMA. To achieve these objectives the work was carried out as follows:

- First of zeta potential tests on different type of aggregate and interpretations;
- Estimation of the zeta potential based on percentage of silica;
- Complex modulus tests on HMA mixed with the same aggregates;
- And finally interpretation and estimation of dynamic modulus based on silica content and rheological properties of bitumen.

2. Materials and Method

2.1. Identification of Aggregates

The aggregates used in this study are basalt of Diack (46% of SiO_2), quartzite of Bakel (94.5% of SiO_2) and limestone of Bandia (0.7% of SiO_2) [6] [7].

2.2. Zeta Potential Test

To measure the impact of the silica on the zeta potential, zeta potential tests on each type of aggregate particles used were performed. During the zeta potential test, electrophoretic light scattering is based on the influence of an electric field applied to a charged particle [8] [9] [10]. The measuring device used in this study is the Zeta-Meter 4.0. It is accompanied by accessories such as an electrophoretic cell, a video set a light beam and a display screen for tracking actions (**Figure 1(a)**, **Figure 1(b)**). During testing, authors noticed that the extreme pH did not allow the measurement of zeta potential. Thus, an approach must be performed to determine the acceptable pH ranges. On the other hand, to have enough available particles in aqueous solutions, fine particles of every type of aggregate were milled (**Figure 1(c)**). Aqueous solutions were prepared using concentrated solutions of acid HCl and base NaOH. These solutions are diluted in distilled water under the control of a pH meter immersed in the solution placed on an agitator (**Figure 1(d)**).

Zeta potential is calculated by the Smoluchowski equation (Equation (1)) [11].

$$ZP = \frac{113000 \times Vt}{Dt} \times EM \quad (1)$$

where EM is the electrophoretic mobility at given temperature ($\mu m \cdot s^{-1}$, $V^{-1} \cdot cm$), Vt is the viscosity of the suspension liquid at the temperature t (poises), Dt is the dielectric constant and ZP is the Zeta potential (mV).

Zeta potential tests were performed on particles of basalt, limestone and quartzite at different pH (acid, neutral and basic). **Table 1** shows the zeta potential test results obtained for basalt, quartzite and limestone at a temperature of 25˚C ± 2. These results indicate that for aqueous solutions at acid pH quartzite Bakel has a positive potential (ZP = +22.58 mV) than the basalt (ZP = +18.87 mV) which is greater than that of the limestone (ZP = +13.32 mV). Which implies that for a given acid solution, limestone will be less capable of electrostatic type bonds that basalt and quartzite which is more likely to build links. At neutral and alkaline pH basalt and quartzite particles have substantially the same

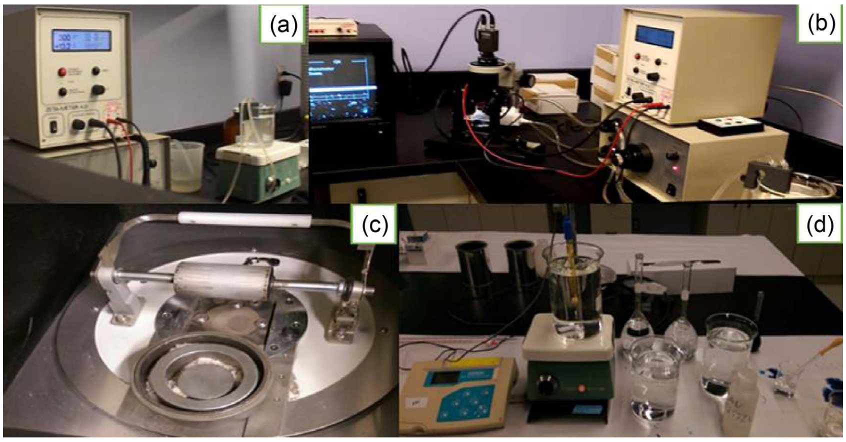

Figure 1. Zeta potential test device, see the end of document. (a) Assembly of the zetameter; (b) Tracing; (c) Crushing of aggregates into fine particles; (d) Dosage of acid solutions; basic and neutral.

Table 1. Zeta potential test results, see the end of document.

Aggregate type	Zeta potential		
	pH = 5.02	pH = 7.12	pH = 9.08
Basalt	19.87	37.07	38.63
Quartzite	22.58	38.52	37.89
Limestone	13.32	16.41	18.66

values with a slight superiority of basalt (respectively +37.07 mV and +38.63 mV; +38.52 mV and +37.89 mV). The limestone has the lowest value with +16.41 mV and +18.86 mV. Which implies that for solutions at pH higher than 7.12 (basic) basalt and quartzite particles will be more able to establish electrostatic bonds that the limestone particles. During the test of zeta potential, two important parameters are measured at the same time by the zetameter. These parameters are the temperature of the solution and the specific conductance. The value of the specific conductance (CS) of an ionic solution depends on the nature of the solution, as well as the geometry of the measurement cell but also the type of anions and cations contained in the solution. It is related to the conductivity, that it depends on the ion concentration, the nature of the ionic solution and the temperature of the solution. The work of De la Roche [12] and highter and Wall [13] have shown that the conductivity depends strongly on the type of aggregate used and the aggregate mixture. Thus, it increases with the density of the aggregate. The change with the bitumen content is very low.

2.3. Complex Modulus Tests

Complex modulus tests were performed at temperatures of 0˚C, 10˚C, 20˚C, 30˚C, 40˚C and 55˚C and for each temperature the frequencies considered are 10 Hz, 3 Hz, 1 Hz, 0.3 Hz and 0.1 Hz. A number of 9 mixtures has been considered including 3 basalt ESG (BDC, BDD, BDF) 3 quartzite ESG (GDC, GDD, GDF) and three simple HMA of limestone (CDC, CDD, CDF) (**Figure 2**).

The analysis of complex modulus test results shows good uniqueness modulus curves for all mixture in the Cole-Cole plane except for the CDF limestone mixture. Indeed, to this mixture the complex modulus test failed by a rupture of the specimen because of its high percentage of voids. **Figure 3** shows that the CDF modulus curve is poorly represented. These results allow us to conclude partially that the HMA mix designed with aggregate with high silica content (≥45% of SiO_2) (BDC, BDD, BDF, GDC, GDD, GDF)give better results than the HMA mixed with aggregate with low silica content (≤1% of SiO_2) (CDC, CDD, CDF).

The development of predictive models in the next section will help us to better explain the impact of silica content on zeta potential of aggregate particles and on the dynamic modulus of HMA. View the temperature variations during complex modulus tests on HMA observed in the laboratory, the dynamic shear modulus test (DSR) tests were conducted at the temperatures and frequencies of

Figure 2. Cylindrical specimens and tension-compression test, see the end of document.

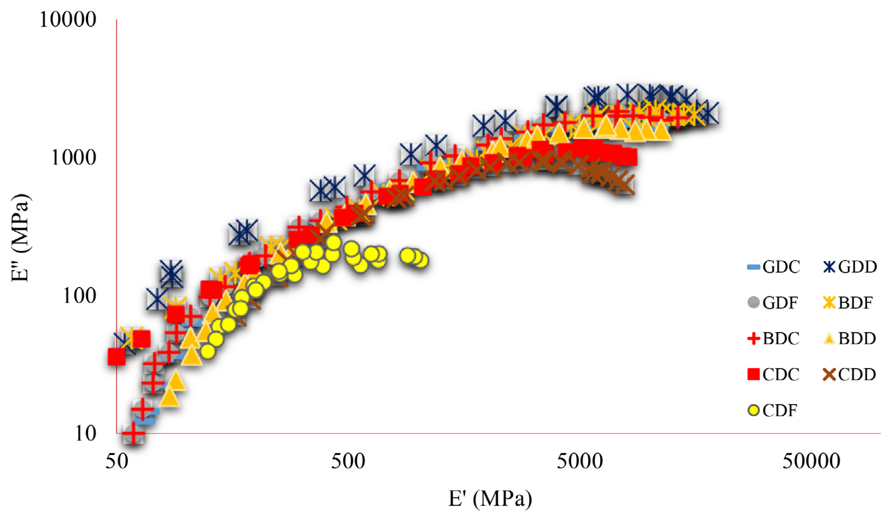

Figure 3. Modulus curves in Cole-Cole plan, see the end of document.

complex module tests on a PG70-16 bitumen grade.

3. Data Analysis

3.1. Estimation of Zeta Potential

For zeta potential predictive model, tests carried out was allowed to collect an amount of 49 data of zeta potential, specific conductance and temperature, 3 percentage of SiO_2, 3 specific gravity and 3 pH.

3.2. Correlation Matrix Analysis

In order to choose the best dependent variables of the predictive model of zeta potential, a correlation matrix was performed (Table 2). Analysis of the matrix shows that the variable specific conductance (SC) was closely linked to the pH and temperature (T) variables, and the variable percentage of SiO_2 was closely linked to the variable specific gravity. Thus, to avoid the phenomena of multi co-linearity, the models developed will consider as variable SiO_2, pH and temperature.

Table 2. Analysis of matrix correlation.

Significant marked correlations at $p < 0.5000$; Number of data = 49					
Variable	SC	pH	Specific gravity	SiO_2	T˚C
SC	1.000000				
pH	**−0.622682**	1.000000			
Specific gravity	−0.060774	−0.161097	1.000000		
SiO_2	0.195547	−0.164509	**0.360844**	1.000000	
T˚C	**−0.630358**	0.073338	0.001876	−0.199054	1.000000

3.3. Development of Zeta Potential Predictive Model

A nonlinear regression mathematical model for zeta potential was developed, and the robustness of the final predictive equation was checked using statistical goodness of fit measures. The final zeta potential predictive model based upon mineral aggregate and solution properties with a total of 49 data points was presented as (Equation (2)):

$$ZP = 139.95148381 + (1.88689007033\text{pH}) + (0.162595092047\text{SiO}_2) - (5.853416601688T) \quad (2)$$

where ZP is zeta potential (mV), pH is the potential hydrogen of solution, SiO_2 represent the percentage of SiO_2 in mineral aggregate and T the temperature (˚C).

Figure 4 shows the analysis of regression with a strong correlation ($R^2 = 0.63$) observed between predicted and measured zeta potential and a low error ($S_e/S_y = 0.38$). To reduce the dispersions in predicting the zeta potential, Fisher's test was carried out on the model. The results show that it is significant with a p-value < 0.005. This mean that the developed model is a good prediction model.

4. Impact of Aggregate Type

To study the impact of the silica content on the prediction accuracy of the models developed, a separated regression was performed in the data depending on the type of aggregate. Remember that all types of aggregate used in this study have different SiO_2 content. Figure 5 shows that zeta potential of Basalt and quartzite with high percentage of SiO_2 are predicted well than Limestone.

5. Verification with an Independent Database

For improve the accuracy of prediction, all the collected database was not used in the development of predictive models. A part composed of 24 samples was retained for model verification by an external database of the database that was used for models development. Figure 6 shows the results. Good accuracy is observed with a $R^2 = 0.64$ and fair $S_e/S_y = 0.69$.

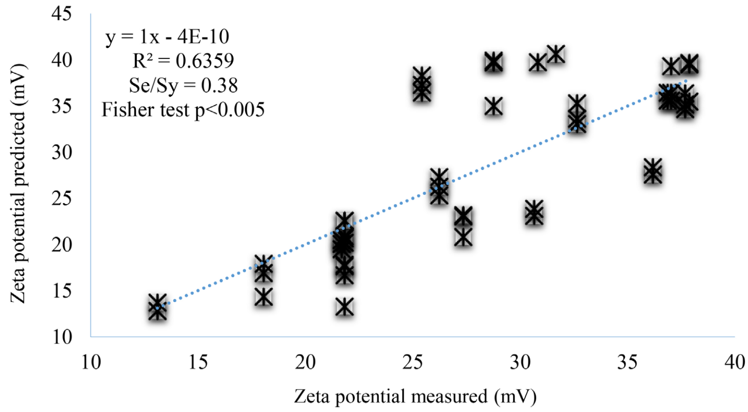

Figure 4. Regression between measured and predicted zeta potential, see the end of document.

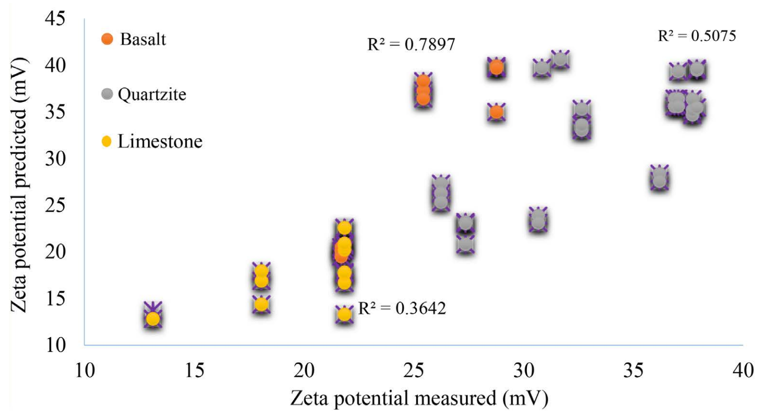

Figure 5. Comparison of the representativeness of models depending on aggregate type, see the end of document.

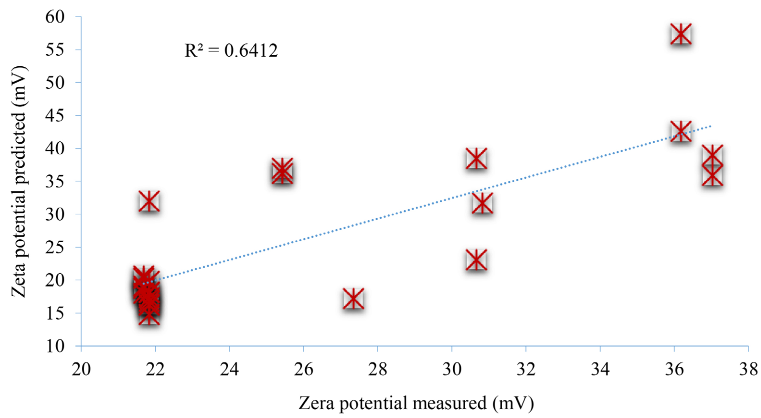

Figure 6. Verification of the model developed by independent database, see the end of document.

6. Sensitivity Analysis of Developed Model

To study the impact of predictor on the model developed, a sensitivity analysis was performed. Thus, for each predictors of a total of 5000 simulations was considered. Figure 7 shows that the zeta potential predicted by the model increased rapidly with the percentage of SiO_2, more slowly with the pH and very little with temperature. Thus, the developed model is more sensitive to the percentage of SiO_2, followed by pH and finally the temperature. Once the main factor influencing the zeta potential (SiO_2) of aggregate particles and thus their adhesiveness properties was identified, a study was conducted to measure its impact on the dynamic modulus of HMA mixed with these aggregates.

7. SiO_2 Impact on the Dynamic Modulus

Analysis of the prediction model of the zeta potential showed that it was highly dependent on the percentage of SiO_2. To measure the impact of this parameter in the measurement and prediction of the dynamic modulus of HMA a study was conducted. During this study were manufactured HMA with aggregate that were used in zeta potential tests. These results allow us to conclude partially that HMA mixed with aggregate with high positive zeta potential give better results than the HMA mixed with aggregate with low positive zeta potential. For dynamic modulus predictive models various tests carried out was allowed to collect an amount of 270 data of dynamic modulus (|E*|) and phase angle (φ) of HMA, shear modulus (|G*|) and phase angle (δ_b) of bitumen, percentage of SiO_2, percentage of void (V_a) and binder content (V_{beff}).

8. Choice of Predictor

In order to choose the best dependent variables of the predictive model, a correlation matrix was performed (Table 3). Analysis of the matrix shows that the variable G* was closely linked to the δ_b and the variable SiO_2 was closely linked to variables V_a and V_{beff}. Thus, to avoid the phenomenon of multicolienarity, the models developed will consider as variable |G*| and SiO_2 or δ_b and SiO_2.

9. Development of Dynamic Modulus Predictive Model

The method chosen for the model development is adaptive Splines method or MARSplines of Data Mining of Statistica software. A regression based on a total

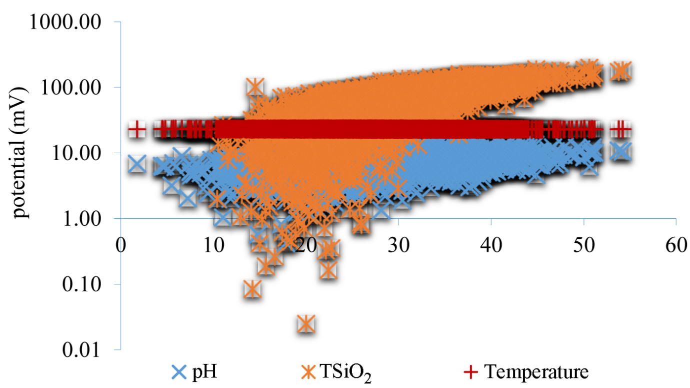

Figure 7. Sensitivity analysis to predictors.

Table 3. Matrix correlation analysis.

Corrélations significatives marquées à p < 0.05000 N = 250							
Variable	T˚C	Hz	Vbeff	Va	δ_b	**SiO_2**	**IG*I**
T˚C	1.000000						
Hz	0.009050	1.000000					
V_{beff}	0.090595	0.003745	1.000000				
V_a	−0.077007	−0.008709	**−0.895515**	1.000000			
δ_b	**0.950722**	**−0.217926**	0.081176	−0.066772	1.000000		
SiO_2	0.060807	0.006097	**0.837554**	**−0.893758**	0.050777	1.000000	
IG*I	**−0.981161**	−0.008726	−0.078763	0.065387	**−0.960966**	−0.050971	1.000000

of several basic functions respectively (function used in the development of the model), 2 independent variables (δ_b and SiO_2 or |G*| and SiO_2), a number of 3 for variable interactions (degree of complexity of the model), a penalty of 2 and a limit of 0.0005 allows to develop the following models (Equations (3) and (4)). Equations presented bellow are respectively δ-SiO_2 and G*-SiO_2 models.

$$\begin{aligned} |E^*|(MPa) = {} & 3.73130653355500e+003 \\ & -1.18464073738361e+002*\max(0;\delta_b-1.98002388719160e+001) \\ & +1.50814129926978e+002*\max(0;\ 1{,}98002388719160e+001-\delta_b) \\ & +5.57621324510587e+000*\max(0;\ SiO_2-7.00000000000000e-001) \\ & \ *max(0;\ 1.98002388719160e+001-\delta_b) \\ & +8.21225936289469e+001*\max(0;\delta b-4.03065338690455e+001) \end{aligned} \tag{3}$$

$$\begin{aligned} |E^*|(MPa) = {} & 3.08518706896302e+003 \\ & +7.37093517729042e+003*\max(0;\ |G^*|\ -5.26651890611619e+000) \\ & -6.05895203964930e+002*\max(0;\ 5.26651890611619e+000-|G^*|) \\ & +8.20780466885278e+001*\max(0;\ |G^*|-5.26651890611619e+000) \\ & \ *\max(0;\ SiO_2-7.00000000000000e-001) \\ & +4.48803248633563e+005*\max(0;\ |G^*|-6.30801551656643e+000) \\ & -9.18661344702369e+003*\max(0;\ |G^*|-5.62726415841968e+000) \\ & -4.93674896362312e+002*\max(0;\ |G^*|-4.15510436360577e+000) \end{aligned} \tag{4}$$

Note: The following models should be used directly with coded predictors 0, 1.

Table 4 shows that for the δ-SiO_2 model, least significant variable is SiO_2 with a frequency of occurrence of 1, followed by variable δ_b of bitumen with a frequency of 4. For the G*-SiO_2 model least significant variable is SiO_2 with a frequency of occurrence of 1, followed by variable |G*| of bitumen with a frequency of 6. It can be deduced that for δ-SiO_2 and G*-SiO_2 model the dynamic modulus of HMA is very linked to the bitumen properties and poorly to SiO_2.

Table 4. Occurrence frequency of predictor.

Occurrence frequency of each predictor		
Predictors variables	**δ-SiO_2 model**	**G^*-SiO_2 model**
δ_b	4	-
$\|G^*\|$	-	6
SiO_2	1	1

Figure 8 shows the regression between the $|E^*|$ measured in laboratory and the $|E^*|$ predicted by δ-SiO_2 and G^*-SiO_2 models. It shows a good correlation for each model with respectively adjusted coefficients of determination of $R^2 = 0.84$ and $R^2 = 0.83$ and low errors $S_e/S_y = 0.38$ and $S_e/S_y = 0.4$. Which means that the developed model allows a good prediction of the dynamic modulus of HMA according to the bitumen properties and the percentage of SiO_2 of aggregates particles.

10. Impact of Aggregate Type

To study the impact of the SiO_2 on the prediction accuracy of the models developed, a separated regression was performed in the data depending on the type of aggregate. Remember that all types of aggregate used in this study have different percentage of SiO_2. Figure 9 shows that $|E^*|$ of HMA mixed with aggregates with highest percentage of SiO_2 (Basalt and quartzite) are predicted well than others (Limestone). On the other hand δ-SiO_2 model better reflects the irregularity observed in the CDF mixture for which the complex modulus test had failed.

11. Verification with an Independent Database

For improve the accuracy of prediction, all the collected database was not used in the development of predictive models. A part composed of 20 samples was retained for model verification by an external database of the database that was used for models development. Figure 10 shows the results. Good accuracy is observed with a good $R^2 = 0.93$ and a fair $S_e/S_y = 0.61$ for δ-SiO_2 model. But, for G^*-SiO_2 model prediction accuracy is very less good with a good $R^2 = 0.788$ and a fair $S_e/S_y = 0.65$. We can conclude that δ-SiO_2 model and G^*-SiO_2 model are good models.

12. Sensitivity Analysis of Developed Models

To study the impact of predictor on the model developed, a sensitivity analysis was performed. Thus, for each predictor a total of 5000 simulations was considered. Figure 11 shows that the dynamic modulus predicted by the δ-SiO_2 model decrease quickly with increasing bitumen phase angle, and more slowly with the percentage of silica. The dynamic modulus predicted by the G^*-SiO_2 model increase quickly with the increasing bitumen dynamic modulus, and more slowly with the percentage of silica.

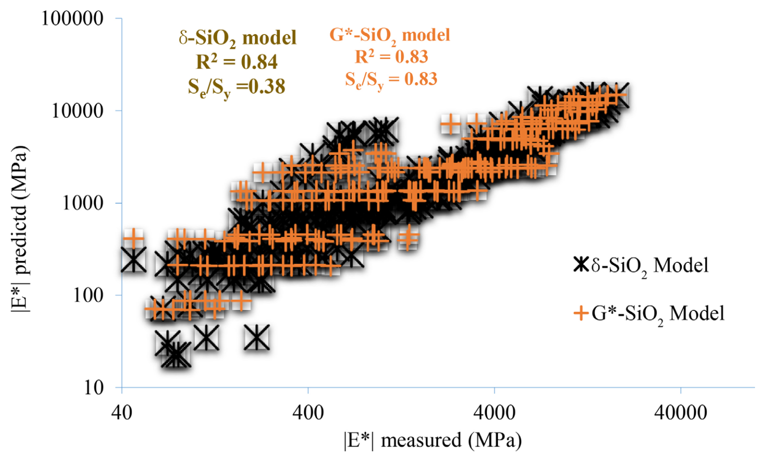

Figure 8. Regression results of |E*| predicted vs |E*| measured for δ-SiO_2 and G*-SiO_2 models.

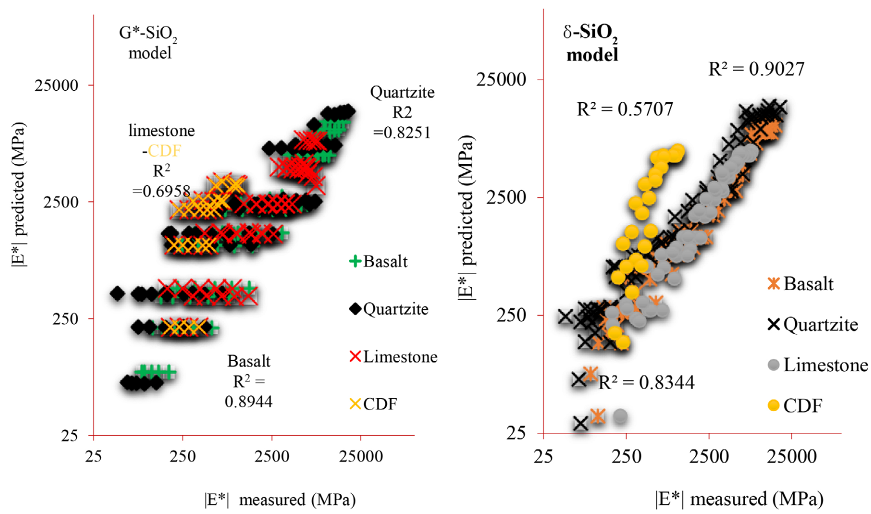

Figure 9. Comparison of the representativeness of δ-SiO_2 and G*-SiO_2 models depending on aggregate.

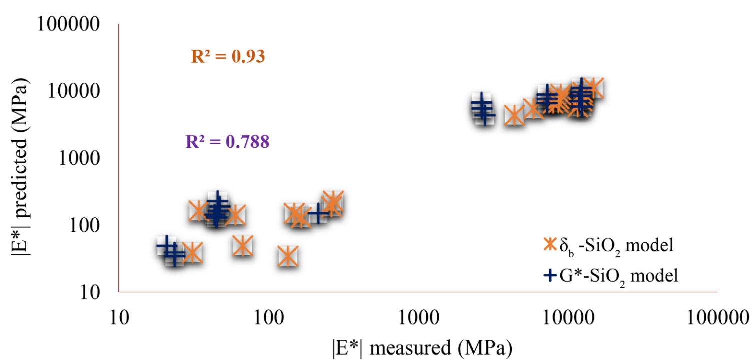

Figure 10. Verification of the model developed by independent database.

This can have a physical significance because many studies showed that the behavior of asphalt was very close to that of bitumen. The work of De la Roche

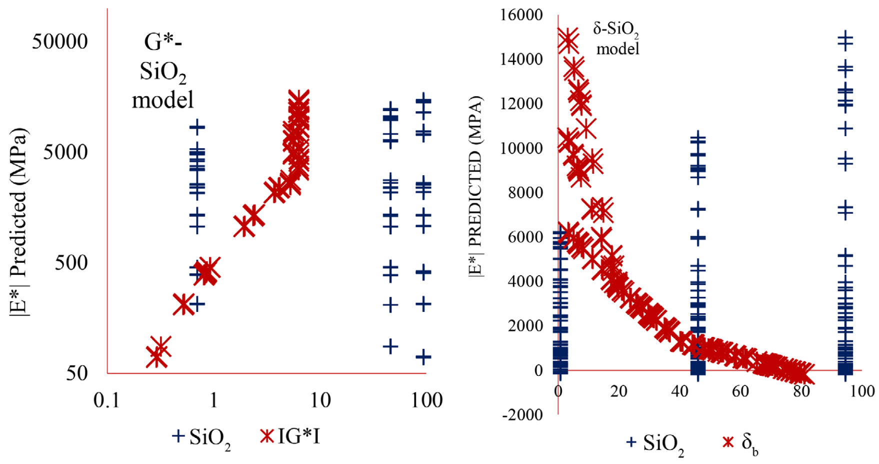

Figure 11. Sensitivity of δ-SiO_2 and G*-SiO_2 models to SiO_2, δ_b and |G*|.

et al. (1997), Bazin *et al.* (1967) and Francken (1977) showed that more bitumen is soft, more it phase angle is high and the complex modulus of HMA is low.An important note is to make on the impact of the percentage of silica. Indeed, at high temperatures and low frequencies (corresponding to the lower modulus values), we observed no significant impact of silica. But at low temperatures and high frequencies (corresponding to the higher modulus values), we observed higher dynamic modulus in HMA mixed with aggregates containing high percentage of silica. This phenomenon is better reflected by δ-SiO_2 model.

13. Conclusion

This study has allowed showing that the zeta potential of e aggregate particles depends on the nature of the rock. The zeta potential test results have shown that the aggregates with high percentages of silica have zeta potentials higher than the aggregates with low percentage of silica. The predictive model of zeta potential developed proven that the silica content is an excellent predictor associated with temperature and pH. The results of complex modulus tests showed that asphalt mixed with aggregates containing high silica content gave better results than those mixed with aggregates with low silica content. Against, the predictive models of dynamic modulus developed shows that it is the rheological properties of asphalt binders that influence more dynamic modulus of asphalt mixtures than silica content at high and medium temperatures. However, the effect of silica is very marked at low temperatures and high frequencies.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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