CaO/Bitumen Nanocomposite: Synthesis and Enhancement of Stiffness Properties for Asphalt Concrete Mixtures

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Abstract— The road-building is complex processes where it enters a lot of factors. Traffic load and climate change are strongly affect road performance. Many researchers are trying to overcome the road distress using the new materials to improve the properties of asphalt. Polymer or crumb rubber was added to the bitumen for a high-quality roads and longer life. This research is concerned with the addition of nano scale materials into bitumen and to study its impact on stiffness properties of bitumen and asphalt concrete mixtures. The bitumen was mixed with CaO nanoparticles at five different modification levels namely 1%, 2%, 3%, 4% and 5% by weight of bitumen. No more 5% CaO nanoparticles was added to the bitumen because no more improvement happens. The result shows a decrease in penetration as well as higher softening point that can lead to improvement in the asphalt binder stiffness. Resilient modulus (Mr) is 1.7 times higher than resilient modulus for unmodified asphalt concrete mixtures. From the limited testing which has been done CaO nanoparticles can be assumed to be used as asphalt additives for hot climate area.

Index Terms— CaO Nanoparticles, Asphalt Concrete, Penetration Test, Softening Point, Resilient Modulus

1 Introduction

Roads are considered the arteries of development in all countries of the world. The basic ingredients in the asphalt concrete pavement are bitumen and aggregate. Bitumen is a visco-elastic material where temperature and rate of load application have a great influence on its behavior. It is believed that the properties of the materials used in the designed asphalt mixtures play an important role in pavement performance [1]. There are many methods that were used to improve the properties of the asphalt such as adding polymers in different shapes and modification level. The primary goal of the using additives to the bitumen is to improve its properties. By improving the engineering properties of bitumen this will be helpful to extent the life span of asphalt concrete pavement. These days, scientists start to use nano materials to improve the properties of bitumen [1-2]. Nano-SiO_2 mixed with styrene butadiene styrene (SBS) was found to improve the viscoelastic properties of the bitumen and have a good impact in the rheologcial properties of the modified bitumen. Using nano polymer modified bitumen improved adhesive properties of the bitumen. Bitumen with high adhesive properties directly improves the bond between aggregate and bitumen. The modified asphalt concrete mixtures with 5% SBS and 2% nano-SiO_2 improve the mechanical properties of the mixture [2:5]. Adding nanoclay to the bitumen improve the resistance to deformation and viscosity of the modified bitumen. On other hand using nanocaly have good impact to improve low temperature carking. Modified bitumen with nanoclay shows excellent fatigue resistance [6-7]. Addition of nano-particles to bitumen have effective role for the bitumen used in hot climate area. That means the modified asphalt with nano-caly can resist rutting [8]. Using carbon nanotubes –Asphalt showed higher stiffness than unmodified asphalt [9-11]. Carbon nano particles added to unmodified bitumen showed increasing in viscosity as well as complex shear modulus which give good indicator that these mixtures can resist rutting. Carbon nano particle improve the rheological properties of modified asphalt binder [12-14]. 15% of nano-sized cement bypass improves the physical properties of bitumen. On other hand using nano bypass increase the compressive strength which give indication that the mixtures can resist rutting [15].

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2. Materials

Asphalt concrete mixtures specimen contains different type of materials including aggregates, bitumen, CaO nanoparticles as bitumen additives.

2.1 Aggregate

Crushed limestone aggregate was used in this study. These mineral aggregates comprised course aggregate (A) with specific gravity 2.64 g/cm^3 and particle size 11 - 16 mm; course aggregate (B) with specific gravity 2.68 g/cm^3 and particle size 4 - 11 mm and fine crushed limestone with specific gravity 2.72 g/cm^3 and particle size < 4 mm. The gradation of the total aggregates mix was obtained by sieve analysis according to the Egyptian Highway Standard Specification (4C). To achieve the required gradations 30 % of coarse aggregate (A) was blended with 30 % of coarse aggregate (B), and 35 % of sand, and 5% of filler, (by weight of total aggregate mix). The gradation of the used aggregate in asphalt concrete mixtures was presented in table (1). Figure (1) presented the gradation of the total mix and specification limits.

ISSN 2229-5518

TABLE (1) GRADATION OF THE USED AGGREGATE ACCORDING EGYPTIAN HIGHWAY STANDARD SPECIFICATION (4C).

Sieve size (mm)	Course aggregate (A)		Course aggregate (B)		sand		Filler		Total Mix.	Specification (4C)	
	%P	30%	%P	30%	%P	35%	%P	5%		lower	Upper
25	100	30	100	30	100	35	100	5	100.00	100.00	100.00
19	90	27	100	30	100	35	100	5	97.00	80.00	100.00
12.50	33	9.9	100	30	100	35	100	5	79.90	70.00	90.00
9.50	4	1.2	87	26.1	100	35	100	5	67.30	60.00	80.00
4.75			30	9	100	35	100	5	49.00	48.00	65.00
2.36			5	1.5	89	31.15	100	5	37.65	35.00	50.00
0.60			1	0.3	50	17.5	100	5	22.80	19.00	30.00
0.30					31	10.85	100	5	15.85	13.00	23.00
0.15					9	3.15	95	4.75	7.90	7.00	15.00
0.075					5	1.75	50	2.5	4.25	3.00	8.00

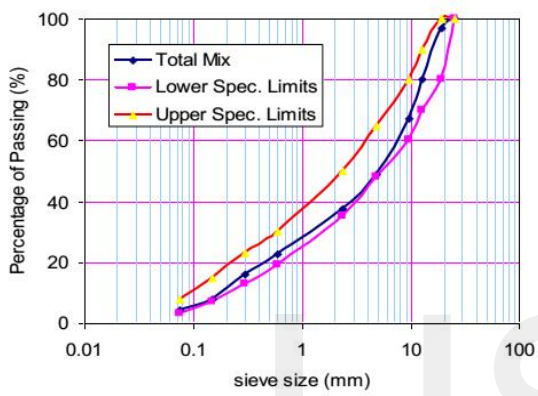

Figure (1) Gradation of the Total Mix and Specification Limits.

2.2 Bitumen

The bitumen used in this study was 60/70 penetration grade obtained from Suez Refinery. The physical properties of the used bitumen are given by the manufacturer and presented in table (2).

TABLE (2): PHYSICAL PROPERTIES OF BITUMEN (60/70) SUEZ REFINERY

Physical properties	Value	Specification limits
Specific Gravity	1.04	1.0 ~ 1.1
Penetration (at 25°C), 0.1mm	63	60 ~ 70
Softening Point, °C	47	45 ~ 55
Flash Point, °C	262	≥ 250
Kinematic Viscosity.(at 135 °C), Cst	327	≥ 320

2.3 Synthesis of CaO Nanoparticles

CaO nanoparticles were synthesized by modified sol-gel route using $CaCl_2.2H_2O$ and NaOH as starting materials [16-18]. In the typical procedure 14.7 g (0.1 mole) of $CaCl_2.2H_2O$ were dissolved in 0.5 liter of distilled water by vigorous stirring. The precursor, $Ca(OH)_2$, was prepared by addition of 1 M NaOH aqueous solution drop wise with vigorous stirring (1200 rpm) to the aqueous solution of $CaCl_2.2H_2O$ at 80 °C. The inert gas (nitrogen) was flowing on the solution surface during 1 M NaOH addition. A white precipitate of $Ca(OH)_2$ was produced over the time. The pH of the solution was adjusted to 11.0 and left under stirring for 6 hours. Then, the precipitate was collected by filtration and rinsed three times with distilled water and dried at desiccator for several hours. The white precipitate was calcined in a muffle furnace at 450 °C for 2 h.

2.4 Structural and Morphology Analysis

X-ray diffraction (XRD) measurements were carried out on dried sample of CaO Nanoparticles to assess the purity of the expected phases and the degree of crystallization and the diffraction angle (2θ) was in the range 20°-80°, as shown in Fig.1. The XRD pattern of the synthesized CaO nanoparticles were recorded by X-ray diffractometer Bruker D8 Advance, Bruker AXS, Germany) and CuK a (λ=1.54056 Å) radiation at 40 kV and 40 mA. Figure (2) shows X-ray diffraction pattern of CaO nanoparticles. The prepared CaO nanoparticles precipitate in cubic phase, which was in consistence with the standard structure of CaO.

Debye- Scherrer's formula (eq.1) has been used to calculate the mean crystalline size of CaO nanoparticles [16, 19]:-

$$D = 0.9\lambda/\beta\cos\theta \qquad (1)$$

Where D is the mean crystalline size (nm), λ is the wavelength of Cu Kα (0.154), β is the full width at half maximum intensity

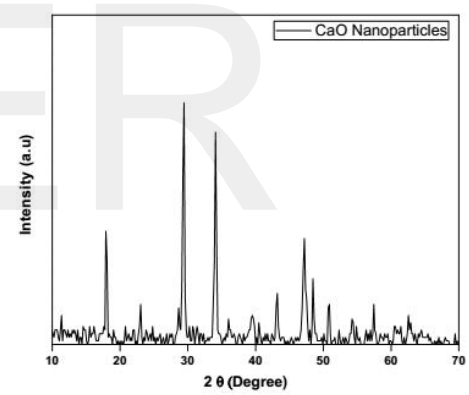

Figure (2) XRD spectrum CaO Nanoparticles.

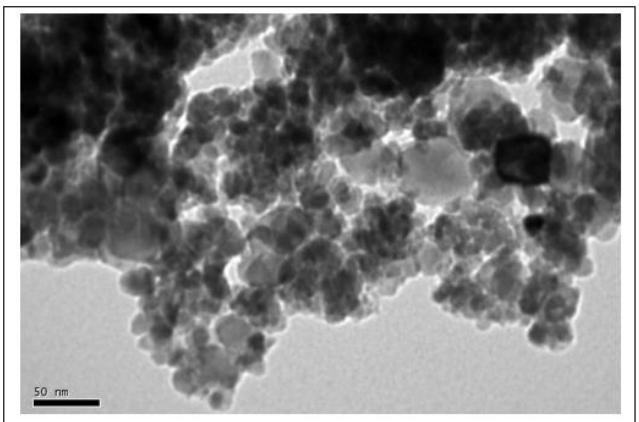

Figure (3) TEM micrograph of CaO Nanoparticles

(FWHM) in radian and θ is the Bragg angle. The mean crystalline size of the CaO nanoparticles calculated to be in the range from 20-30 nm. The morphology of CaO nanoparticles was analyzed using transmission electron microscope (TEM) as shown in figure 3, TEM image of Ag nanoparticles revealed crystalline, free-standing, and approximately spherical particles as well as a number of aggregates.

3. Preparation of modified samples

3.1 Preparation of modified CaO/bitumen Nanocomposite

Firstly the bitumen is heated alone to a 170 °C then the required amount of CaO nanoparticles (by weight of bitumen in asphalt concrete mixtures) is added to the heated bitumen to get the modified bitumen blend. A low shear mechanical mixer with speed of 700 rpm was used for 30 min to produce the homogeneous blend. After this the bitumen is heated again for 5 minuets then it is used for mixing with aggregate and filler.

3.2 Preparation of asphalt concrete mixtures

Marshall method of mix design is used to prepare Marshall specimens which is used in all asphalt concrete mixtures mixtures test. Aggregates and the bitumen were heated in the oven, trial specimens were prepared in laboratory at five different asphalt contents 4%, 4.5%, 5%, 5.5% and 6%. Three specimens were prepared for the same bitumen content and the average of the test result was taken. The optimum bitumen content is selected based on stability, unit weight, and specified percent air voids in the total mix. The optimum bitumen content (5%) is selected as the average bitumen content for maximum stability, maximum unit weight, and specified percent air voids in the total mix (4%). This optimum content was used for both control and modified asphalt concrete mixtures.

4. Characterization of Bitumen and Asphalt Concrete Mixtures

Different test were used to evaluate the properties of modified and unmodified bitumen and mixtures. Penetration and softening point are used to evaluate the properties of control and modified bitumen. The mechanical properties for control and modified asphalt concrete mixtures were evaluated using diametral resilient modulus test and repeated load deformation. The analysis of test result shows various characteristics of modified and unmodified asphalt concrete mixtures.

5. Results and Discussions

5.1 Penetration Test

Penetration test was used in this research for modified bitumen and unmodified bitumen.

In this test the consistency of a sample of bitumen can be measured by determining the distance in tenths of a millimeter that a standard needle vertically penetrates the bitumen specimen. Water bath was used to maintain the temperature of specimen and the temperature was 25 °C (ASTM D 5-97) [20]. Figure (4) presented the result of penetration test and form the figure it can be seen that adding CaO nanoparticles materials improve the penetration properties of modified bitumen. The value of penetration for modified bitumen with 5% CaO nanoparticles was decreased by 28.9%. Lower penetration grade is preferred in hot climate area.

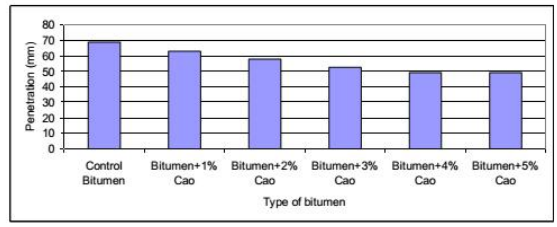

Figure (4): Penetration test result for modified and unmodified bitumen

5.2 Softening Point

To determine the softening point of bitumen within the range 30 to 157 °C by means of the Ring-and-Ball apparatus (ASTM D36-95) [21]. Adding Cao affect the Softening point at all modification level. The softening point increase with the increase of cao present and this is assumed to be good indicator for resistance to high temperatures. The stiffness of the materials affects by temperate and if the used bitumen has resistance to high temperature this will lead to improve the pavement performance. The value of softening point was increased by 24.5 % when 5% of CaO nanoparticles were added to unmodified bitumen. Figure (5) presented all result for softening point for modified and unmodified bitumen.

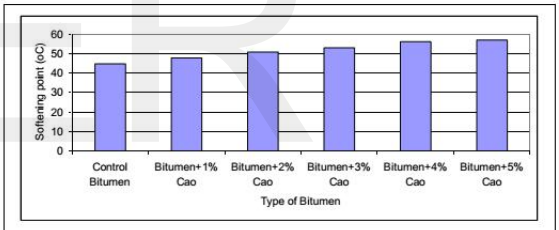

Figure (5): Softening point test result for modified and unmodified bitumen

5.3 Diametral Resilient Modulus (Mr)

The resilient modulus test (Mr) is used to measure the stiffness of asphalt concrete mixtures. The test was run according to (ASTM D 4123 - 82.) to compare between the stiffness of all studied mixtures. Resilient modulus test (Mr) is one of the most important input in flexible pavement design. The resilient modus test measure the pavement response in terms of dynamic stresses and corresponding strains. The result of resilient modulus is used to evaluate the quality of the used materials in the mixtures as well as important input for asphalt concrete pavement design. The resilient modulus gives good indication to compare between the changes of the materials stiffness at different modification level when a sample is exposed to cyclic loading [22,23]. Equation (2) was used to calculate the resilient modulus for all tested sample.

$$Mr = \frac{P(\mu+0.27)}{(t)(\Delta H)} \qquad (2)$$

where:

Mr = asphalt concrete resilient resilient modulus test (Mr), N / mm^2

P = Maximum applied force (N)

μ = Poisson's ratio

t = thickness of sample, mm

ΔH = Recoverable horizontal deformation, mm

Figure (6) presented the test result of resilient modulus (Mr). It is clear that by increasing of modification level the resilient modulus increased. The increasing in resilient modulus means that there is improvement in the stiffness of the modified tested materials. Resilient modulus for modified mixtures with 5% (CaO nanoparticles) is 1.7 times higher than that for unmodified mixtures. No big difference in the result for modified mixtures with 4% CaO nanoparticles than modified mixtures with 5% CaO nanoparticles because of this no more CaO nanoparticles was added to bitumen.

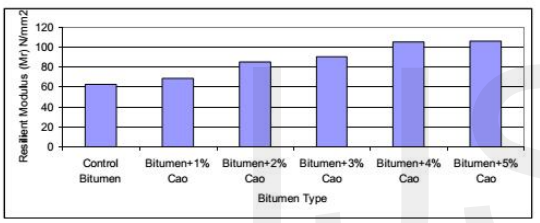

Figure (6): Resilient modulus test result for modified and unmodified bitumen

6. Conclusion

This study presents and discusses the results of penetration tests, softening point and resilient modulus tests conducted on bitumen and asphalt concrete mixtures with different contents of CaO nanoparticles, to evaluate the effectiveness of CaO nanoparticles as an asphalt modifier in road construction works. The benefits of using nano materials in asphalt mixtures increase the effective volume of the binder which helps to make thicker film of binder which increases the intensity of interdependence between aggregate particles. The penetration of the modified bitumen decrease with the incease of nano-Cao level in the bitumen, this result improves directly the resistance of the asphalt concrete mixtures to hot climate area. In the same case scoffing point increase with the increase of the nano-Cao level in the bitumen which give real indicator that the modified bitumen can resist high temperature. On the other hand the resilience modulus is higher 1.7 times for the modified mixtures with 5% nano-cao that means real improvement in the stiffness of modified mixtures. Finally CaO nanoparticles can be used to modify the bitumen which will be used in hot climate area.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the support offered by South Valley University in providing the facilities for the experimental work in this paper.

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