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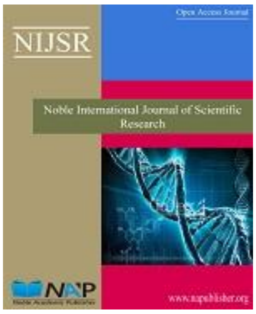

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INFLUENCE OF NANO MATERIAL ADDITIVE ON SURFACE FREE ENERGY (SFE) OF ASPHALT BINDER

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ABSTRACT: One of the essential properties of asphalt binder is the resistance to moisture damage. Therefore, implementation of nano material additive can control and improve the resistance to moisture damage of the asphalt pavement, change the temperature susceptibility characteristics, and create a new material with different physical and rheological properties. In this investigation, one type of Nano material (silica fume) was mixed in different percentages with (40-50) penetration grade asphalt cement binder. The resulted modified asphalt cement was subjected to static contact angle measurements and determination of surface free energy components of the binder using three types of probe liquids and Sessile drop technique and with the aid of equations of work of adhesion. A digital camera has been implemented to capture the image of the drop of liquid formed over the surface of a glass slide coated with asphalt cement. The captured images were transferred to the image processing software (Comef. 4.7) to determine the static contact angle. It was observed that these contact angles vary according to the type of probe liquid, and percentage of Nano materials added to asphalt cement. It was concluded that adding one and two percent of Nano material to asphalt cement has implies an increment in the surface free energy of the binder by 28.8 % and 18.4 % respectively, while the implementation of three and four percent of silica fume into the binder exhibit a reduction in surface free energy by 21.3 % and 24.2 % respectively. However, the change in contact angle was fluctuating and not significant.

Keywords: Asphalt cement; Nano material; Silica fume; Surface free energy; Contact angle.

1. INTRODUCTION

Research work dealing with the improvement of asphalt cement binder by adding organic or inorganic Nano-filler materials are going on globally to optimize the production, processing, and testing capabilities as stated by Partl, et al. [1]. Nano material should improve long-term performance and functional properties of the materials in a significant way without reducing the clear advantages of existing asphalt pavement materials as declared by Livingston [2]. Sarsam [3] addressed that the surface free energy of the binder is defined as an amount of work required for creating unit area of the material in vacuum. It governs the ability of the binder for wetting of aggregates with a thin film of asphalt binder. Derun and R. [4] proposed a surface free energy (SFE) method to assess the influence of various additives on moisture susceptibility of asphalt concrete mixtures. Two nano-material additives are selected and blended with the neat asphalt to fabricate modified asphalt binders. The SFE components of these modified asphalt binders are measured.

The ratio of adhesion of asphalt-aggregate to that of asphalt-aggregate-water, was calculated and implemented to rank the asphalt mixtures in terms of their moisture susceptibility performance. Kakar, et al. [5] addresses the use of chemical surfactant additive to prepare asphalt binder and considers the use of surface free energy evaluation as a fundamental material property to assess mixture performance. The contact angle measurements were determined to evaluate surface free energy parameters such as work of adhesion, work of debonding and compatibility ratio. The results show that the use of the additive reduces surface free energy and slightly improves the work of adhesion. Moreover, the additive improves the spreadibility of asphalt binder over the aggregate particles. Arulraj and Carmichael [6] stated that the influence of filler particles on the cement binder increases with decreasing size to (nano scale) of the filler particles.

However, only rough instructions are given on the dosage such as the acceptable content of filler. Such dosage concerns mainly on overall gradation of asphalt concrete mixture. An investigation by Rahmad, et al. [7] on Surface free energy as determined by sessile drop device shows that addition of different percentages of additive could initiate dissimilar implications on surface properties.

The additive had improved the adhesion characteristics of modified binders. It was concluded that the adhesive characteristics of the blending are at its best and the additive had significant effect on the adhesion and stripping behavior. Parviz [8] stated that the thickness of binder films between the mineral particles in a pavement is mostly in the order of a micrometer or even below, and one could think of measuring the properties of mixes of fillers and binders since the behavior of these materials deviates fundamentally from pure binders and be the first step from the pure binder towards the composite material asphalt. You, et al. [9] reported that Nanoparticles for pavement materials must be non-hazardous, low-cost products, which are easy to handle and available. They should also fulfill ecological requirements such as low energy consumption and environmental compatibility.

This is considered a very positive factor in terms of sustainability. Surface to volume ratio of Nano materials is one of the important properties of materials produced at the Nano scale as stated by Arabani and Hamedi [10], and the work by Ghasemi, et al. [11]. At this scale the behavior of bulk material behavior is dominant. Azarhoosh, et al. [12] studied the components of the free energy of the adhesion at the interface of the asphalt binder and aggregate using asphalt binder with a penetration grade of 85/100 and Nano lime as its modifier. It was noted that the use of Nano lime has increased the base component and decreased the acid component of SFE. However, the use of nanomaterial also increases the total SFE of modified asphalt binder. it was concluded that the use of Nano lime increases the free energy of adhesion at the interface of asphalt binder and aggregate.

In other study conducted by Azarhoosh, et al. [13], the effect of two types of Nanomaterial (nano-TiO_2 and nano-ZnO) on fatigue behavior of mix asphalt was evaluated. The results indicated that asphalt modified by Nanomaterials exhibit more resistance to fatigue failure due to improved cohesion and adhesion in the asphalt binder systems. The impact of three types of Nano materials on stripping potential of asphalt concrete has been investigated by Sarsam and AL-Azzawi [14].

The effects of using different percentages of nano zinc oxide on fatigue cracking of asphalt mixtures have been evaluated by Azarhoosh, et al. [15]. The mechanism that affects the asphalt cement's cohesion and the adhesive bond between aggregate and AC were determined using the surface free energy (SFE) method. The results showed that adding nano Zink oxide leads to decrease the acid component of SFE and increase of the basic component in SFE of the binder which enhances the adhesion between the aggregate and binder.

Furthermore, the asphalt mixtures that contain nano additive showed greater fatigue life than the control mixtures due to improved cohesion energy and higher resistance to fatigue cracking in asphalt film. The influence of the particle size distribution of fillers was given only little attention, in common practice, so far, there are considerable differences in the particle size distribution of different fillers. Nano-Filler particles are particles smaller than 0.09 mm as explained by Bhasin, et al. [16]. With simple methods, like sedimentation or washing method, the grain distribution of filler ranging between 1µm up to [0.09 mm] can be determined on a routine basis but are not commonly used in asphalt technology. SFE components, and work of cohesion of the matrix asphalt and modified asphalt with alumina trihydrate were investigated by Liu, et al. [17] using the SFE approach. The static contact angles were measured to calculate the SFE parameter. It was concluded that the addition of alumina trihydrate had increased the contact angle, van der Waals component, total SFE, and cohesion energy, but decreased the acid base component for all binder samples. However, the work of adhesion of all asphalt aggregates increased due to additive, but the work of debonding decreased.

Hamedi and Esmaeili [18] investigated the effects of two nano anti-stripping additives called nano iron oxide (Fe_2O_3) and nano aluminum oxide (Al_2O_3) on the moisture susceptibility of hot mix asphalt (HMA) mixtures containing crushed glass. The results showed that the addition of nanomaterials had improved the adhesive force between asphalt binders and aggregates by reducing the acidic and increasing the basic properties of the modified asphalt binder. Moreover, implementation of nanomaterials also increased the initial energy required to separate asphalt binder from the aggregate surface and reduced the risk of moisture damage by increasing the total SFE of asphalt binder.

The aim of this research work is to verify the influence of Nano material (silica fume) on the surface free energy of asphalt cement binder and the contact angles with prob liquids with the aid of Sessile drop method. The surface free energy could be implemented in the evaluation of the moisture susceptibility of binder and control the stripping which are considered an essential parameter for paving asphalt binder.

2. MATERIALS PROPERTIES AND TESTING METHODS

2.1. Asphalt Cement

Asphalt cement binder with penetration grades of 40-50 was obtained from Dourah refinery, Baghdad, and was implemented in this investigation; Table 1 illustrates the physical and rheological properties of asphalt cement.

Table 1. Physical and Rheological Properties of Asphalt Binder as per ASTM [19].

Property	Units	Specification	Results for grade (40-50)
Penetration	0.1 mm	ASTM D-5	46
Softening point	˚ C	ASTM D-36	51
Ductility	Cm	ASTM D-113	128
Specific gravity	--------	ASTM D-70	1.042
Flash point	˚ C	ASTM D- 92	310
Viscosity	Poises	ASTM D-2171	4046×10^3
Penetration index	----------	Shell nomograph	- 0.0228
Stiffness modulus	N/m^2	Shell nomograph	1.0×10^8
After thin film oven test ASTM D- 1754			
Penetration of Residue	0.1 mm	ASTM D-5	31
Ductility of residue	Cm	ASTM D-113	83
% loss in weight	%	SCRB, 2003	0.175

Source: Laboratory tested by the researchers

2.2. Nano Material

One type of Nano material (silica fume) was implemented for this investigation, it was manufactured by Wacker Silicon Company in Germany as fluffy powder and obtained from local market; Table 2 shows its physical properties. Table 3 exhibit the chemical composition of silica fume.

Table 2. Physical properties of silica fume

Maximum sieve size	PH value	Density, kg/m^3	Specific surface area, m^2/kg
Passing 75 µm retained on 40 µm	4.5	202	200000

Source: Laboratory tested by the researcher

Table 3. Chemical composition of Nano material (silica fume)

Chemical composition, %	Silica Fume
SiO_2	99.1
Fe_2O_3	35 ppm
Al_2O_3	0.03
CaO	0.03
MgO	52 ppm
Loss on ignition	0.70

Source: Laboratory tested by the researcher

Asphalt cement was heated to 160 ˚ C in an automatic controlled oven, and then poured into 50 grams capacity aluminum cans. The required amount of Nano material (silica fume) was introduced gradually with continuous mechanical stirring. The stirring process was continued for 60 minutes at the same mixing temperature of 160 ±2 ˚ C to insure homogeneity of the mix. Four different percentages of Nano material have been introduced starting with 1% with constant increments of 1%. A glass slides of (25.4 x76.2 x 1) mm dimensions were heated, and then submerged into the molten modified asphalt binder to a depth of approximately 15 mm, the excess binder could drain from the slide until a very thin film of binder of (0.18 to 0.35 mm) thickness, and uniform layer remains on the slide. The thickness of asphalt binder was kept uniform on both sides of the slide throughout its width. Finished slides were stored in vertical position from the end of coated slides and placed in cork box and allowed to cool to room temperatures as shown in Figure 1.

The surface free energy of the modified asphalt cement has been measured using drops of three types of probe liquids recommended to be used in this test. These are deionized water, glycerol (base), and Formamide (acid). A probe liquid is dispensed over a smooth horizontal surface coated with asphalt binder. The image of the drop of liquid formed over the surface of the binder is captured by using a digital camera. Contact angles are obtained by analyzing the image using image processing software (Comef.

4.7) software. A static Contact angles measured with different probe liquids are used with equations of work of adhesion to determine the three surface energy components of the asphalt binder as per Little and Bhasin [20].

A total number of 12 slides were perpetrated for this technique. A drop with a contact angle over 90 degrees is considered as hydrophobic case according to Tan and Guo [21], and Bhasin, et al. [16]. This condition is exemplified by poor wetting, poor adhesiveness and the solid surface free energy is low. However, A drop with a small contact angle is considered as hydrophilic case; this condition reflects better wetting, better adhesiveness, and higher surface energy. Figure 2 exhibits the Schematic diagram of Sessile drop technique.

Figure 1. Prepared Glass slides technique

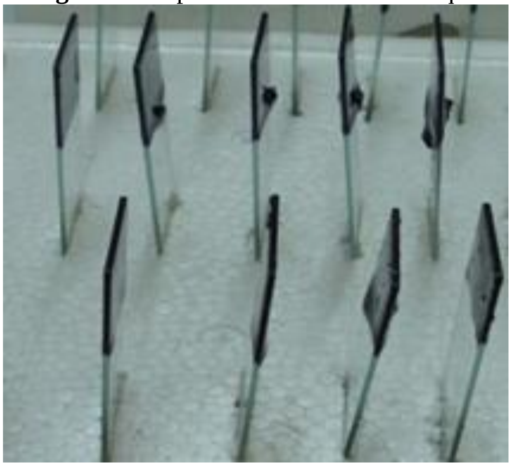

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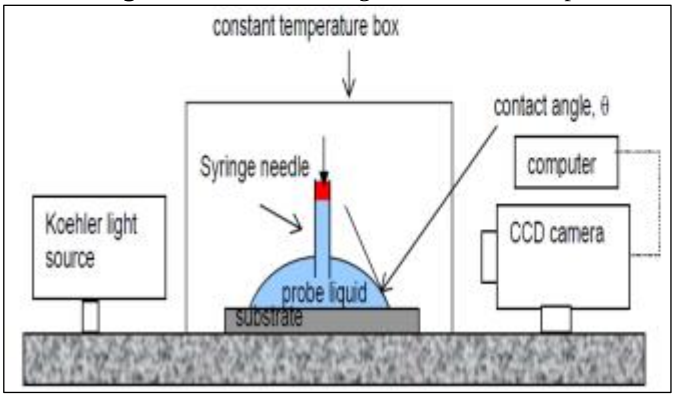
Figure 2. Schematic diagram of Sessile drop



Source: Laboratory tested by the researcher

The surface free energy component of a solid surface is determined by measuring its contact angles with various probe liquids. Contact angles were measured for at least three replicates with each probe liquid for each percentage of Nano material additive. Table 4 exhibit the surface free energy components of the implemented probe liquids.

Table 4. Surface free energy components of the probe liquids, Little and Bhasin [20].

Probe Liquid	Lifshitz-van der Waals γ^{LW}	$\gamma +$ Acid	$\gamma -$ Base	γ Total surface free energy (ergs/cm^2)	Density g/cm^3
Water	21.80	25.5	25.50	72.80	0.997
Formamide	39.00	2.28	39.60	58.00	1.134
Glycerol	34.00	3.92	57.40	64.00	1.258

Source: Laboratory tested by the researcher

3. RESULTS AND DISCUSSIONS

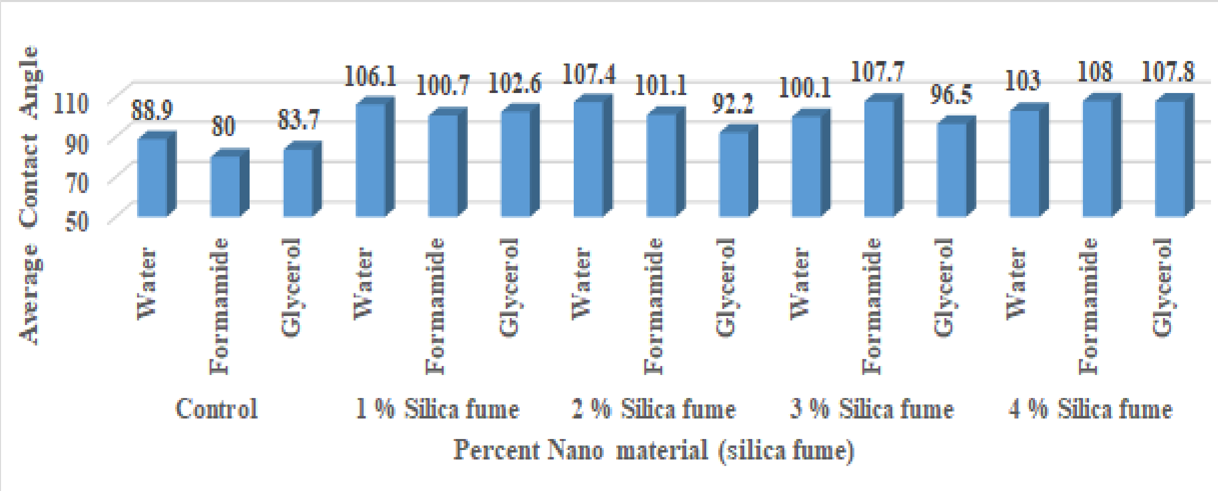
3.1. Influence of Nano Material on Contact Angle

Figure 3 presents the scatter of average contact angle for the control asphalt binder (without additive) and for modified binder. The results for control asphalt are approximately in the range of 80.01 to 88.95 degrees. These results reflect better wetting and better adhesiveness, and the asphalt exhibits hydrophilic behavior. By adding different percentages of Nano material to asphalt binder, the average contact angle was increased to the range of 92.23 to 108.02 degrees for all types of probe liquids. It can be noted that the contact angle for the deionized water component increases in a range of 12.3 % to 20 % when silica fume was implemented in the binder.

The acid component (formamide) exhibits an increment in contact angle in a range of 25.8 % to 35 % after implementation of the Nano material. However, the base component (Glycerol) exhibits an increment in the contact angle in the range of 10.1% to 28.7 % after implementation of silica fume. These results reflect poor wetting and poor adhesiveness, and the behavior changes to hydrophobic. However, the overall changes in contact angle were fluctuating and not significant. Similar findings were reported by Bhasin, et al. [16].

The contact angle could directly indicate the wetting ability of the probe liquid with a solid. Generally, if the contact angle is close to zero, the solvent spreads completely on the surface; conversely, the contact angle more than 90° indicates that the solvent is not wetting or is poorly wetting the surface; and if it is in the range from 0° to 90°, it nicely wets the surface of the material as addressed by Liu, et al. [17]. The contact angles were more than 90° when the deionized water was implemented as the probe liquid for all Nano material dosages, indicating that the water cannot wet them well. Furthermore, the use of higher amounts of 3 % silica fume was found to possibly reduce the contact angle.

Figure 3. Influence of Nano material on contact angle of asphalt binder



Source: Laboratory tested by the researcher

3.2. Influence of Nano Material on Surface Free Energy of the Binder

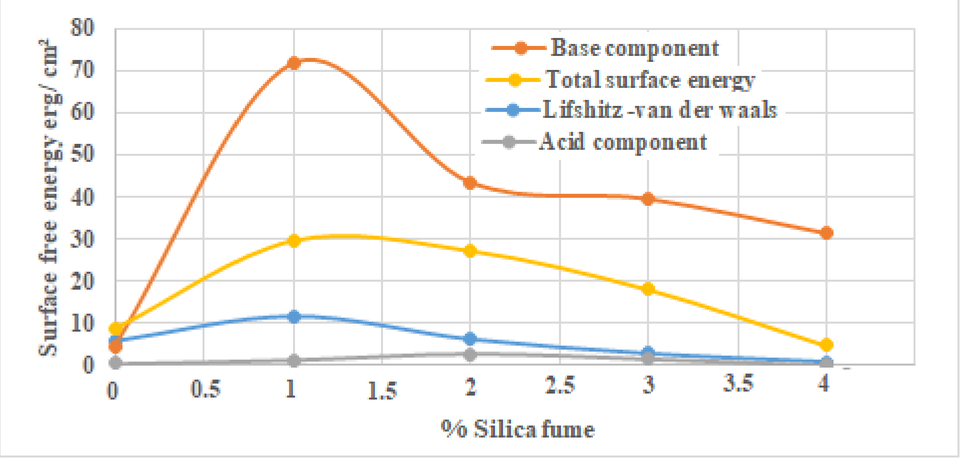
Figure 4 demonstrates the variation of acid, base, and deionized water components of surface free energy by the addition of silica fume. It can be observed that the addition of one and two percentages of Nano material to the asphalt cement had increases the total surface free energy of the binder by 28.8 % and 18.4 % respectively. However, the implementation of three and four percentages of silica fumes causes poor wetting and poor adhesiveness, and the behavior changes from hydrophilic to hydrophobic as the surface free energy decreases by 21.3 % and 24.2 % respectively.

It can be noted that the acid component provides the lower contribution and the deionized water exhibit higher influence in the total SFE, while the base component provides the highest contribution in the total surface free energy for control binder. The results shown in Figure 4 indicate that the polar component (acid and base) of the asphalt binder is very small compared with that of the nonpolar (deionized water) component. Therefore, considering that a large portion of the total SFE of the asphalt binder is formed by the nonpolar component, its expected bond with other materials such as aggregates is said to be mainly due to a nonpolar component and covalent bonds. As the percentage of silica fume increases, the surface energy components also increase up to 2 % of silica fume.

Further increments in Nano material exhibit a dramatic reduction in the SFE component as well as the total SFE. In addition, the use of Nano material has led to a significant increase in the base component and a minimal increase in the acid component of the modified asphalt binder, which is associated with an increase in the total SFE and its expected resistance to the cohesion fracture. On the other side, the use of Nano material also increases the nonpolar component of the modified asphalt binder. This increase is associated with increasing the base and decreasing the acid components of the modified asphalt binder, which can improve the adhesion of this type of asphalt binder to aggregates. However, the increase in the nonpolar component is low relative to polar component (base).

As a result, the modified asphalt binder, which has greater free energy, is expected to be more resistant to the fatigue failure resulting from the cracks in the asphalt binder's membrane. Such finding agrees with the work reported by Sarsam [3]; and Little and Bhasin [20]. Such behavior refers to the optimum silica fume content of 1% which can control the stripping of binder and provide proper wetting of aggregates with asphalt binder. It can be concluded that the use of Nano material has increased the base component and decreased the acid component of SFE. The use of Nano material has led to an increase in the total SFE of modified asphalt binder, which will increase the amount of energy needed for cracking in the asphalt binder. Similar findings were reported by Azarhoosh, et al. [15].

Figure 4. Influence of silica fume on surface free energy of asphalt cement.



Source: Laboratory tested by the researcher

4. CONCLUSIONS

Based on the limitation of materials and test program, the following conclusions are drawn:

1- The addition of one and two percent of Nano material to asphalt cement has implies an increment in the surface free energy of the binder by 28.8 % and 18.4 % respectively.
2- The implementation of three and four percent of silica fumes causes poor wetting and poor adhesiveness, and the behavior changes from hydrophilic to hydrophobic as the surface free energy decreases by 21.3 % and 24.2 % respectively.
3- The change in contact angle was fluctuating and not significant.
4- Implementation of the surface free energy concept using Sessile Drop technique should be considered when the stripping of asphalt concrete is under question.
5- The addition of Nano material (silica fume) is recommended to control the moisture susceptibility of the asphalt concrete mixture.

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