Innovative Nano-engineered Asphalt Concrete for Ice and Snow Controls in Pavement Systems

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ABSTRACT

Each year transportation agencies go through difficulties for ice or snow removal from the roadways and airport paved surfaces in cold regions. Presence of snow or ice on the paved areas can cause traffic accidents and financial loss from flight cancellations or delays. For overcoming the problems associated with winter pavement maintenance, the use of superhydrophobic (super water-repellent) coating techniques is gaining attention as a smart and cost-effective alternative to traditional snow and ice removal practices. This study focused on creating, characterizing, and evaluating innovative superhydrophobic coatings on asphalt concrete surfaces for ice- and snow-free flexible pavement applications. The Layer by layer (LBL) method was utilized to create asphalt concrete surface coating with the polytetrafluoroethylene (PTFE) as a well-known super ice/water-repellent material. Superhydrophobicity of the coated asphalt concrete surface was characterized in terms of the water-contact angle. This property was evaluated for different test variables including spray times and dosage rates of PTFE under a statistical design based experimental test program. The results of statistical analyses indicate that the spray time and dosage of PTFE significantly affect the ability of a coated flexible pavement to be icephobic/superhydrophobic. Based on the results obtained from statistical analysis, asphalt concrete samples representing the surface texture of flexible pavements were coated using LBL method. Using a British pendulum tester the performance of coated samples were evaluated against skid resistance. The measurement results indicate that uses of the LBL method for spray depositing the PTFE particles is a promising method for achieving icephobicity, and British pendulum tester can reflect the change effect of the PTFE dosage over the coated asphalt concrete in terms of skid resistance.

Keywords: Asphalt, De-icing, Friction, Surface Texture, Testing

1. INTRODUCTION

Annually, in cold regions, huge amounts of money are spent solely for the purpose of ice or snow removal from the surface of roadways and airport paved surfaces like runways, taxiways, aprons, etc. Presence of ice and snow on the paved areas can cause traffic accidents and financial loss due to flight delays or cancellations. For mitigating the problems associated with ice/snow formation on the surfaces paved with asphalt concrete, superhydrophobic (super water-repellent) coating techniques [1] have received recent attention as an alternative to traditional snow and ice removal practices. A surface is called superhydrophobic, when the contact angle of droplets deposited on it are equal to or bigger than 150° [2]. In this case, the water droplets do not wet the surface and can easily roll off when they are blown or when the surface is tilted. Combination of surface roughness and low surface energy can result in superhydrophobicity [3]. Roughness effect is explained through using two distinct models: Wenzel and Cassie models [4]. According to the former model, roughness – at micro level - increases the surface area of the solid which geometrically improves the hydrophobicity. However, the latter model explains that if nano-roughness is added to the micro-roughness, the hydrophobicity will be further increased. According to Cassie model, air can remain trapped beneath the water droplets. Tiny entrapped air pockets reduce the solid-liquid contact area making the surface superhydrophobic. If the two aforementioned models are applied for roughness induction in certain types of hydrophobic materials with low surface energy, the final products will be superhydrophobic. Polytetrafluoroethylene (PTFE) with a water-contact angle of 108° [5,6] is a hydrophobic material having low surface energy; PTFE particles with diameters at submicron length scales can readily become superhydrophobic with applying an appropriate deposition technique [5].

The primary advantage of using superhydrophobic nano-coatings with icephobic properties is that it reduces or prevents the ice/snow accumulation more economically and time efficiently than traditional snow and ice removal practices [7–10]. There is very limited literature dealing with applying nanomaterials on asphalt concrete in order to make it ice/water repellent. For the first time, using wet chemistry method, a copolymer fluoroacrylate previously modified with CaO nanoparticles was sprayed over the asphalt concrete; the results revealed that the coated asphalt concrete was able to curb the formation of ice on the surface [11]. In addition to making surface superhydrophobic, PTFE is one of the well-known materials for reducing ice adhesion strength because of its low surface energy and chemical stability [12]. PTFE's icephobicity has been widely investigated on different substrates like plastic [13] and aluminum [14]. However, the ice/water repellency of PTFE has not ever been evaluated on asphalt concrete.

After applying the super water-repellent (superhydrophobic) materials on the surface of pavement, skid resistance must be controlled. There are two components affecting the tire-pavement friction [15]: the adhesion developed between the pavement surface and tire, and the aggregate micro-asperities penetrating into the tire rubber. The former develops due to electrostatic attraction between the rubber molecules and the asperities on the pavement surface. The latter is the result of rubber deformation hysteresis. The asperities of the pavement surface are classified into different levels: micro-texture, macro-texture and mega-texture [16,17]. Among various test types on surface characterization of pavement surface, British pendulum test has been considered as a standardized test for practical applications [18]. The British pendulum number (BPN) measured on the surface of asphalt concrete is considered to be a good measure of its skid resistance. Measured BPN has contribution to skid resistance at both low and high speeds, and the physical properties of aggregate are the predominant factor at high speeds - whether the surface is coated or not.

In this study, a statistical design based experimental test program was developed to create and evaluate the superhydrophobic coatings on asphalt concrete for ice- and snow-free flexible pavement applications. The Layer by layer (LBL) method was utilized to make asphalt specimens/substrates coated with PTFE nano-particles at different spray times and with variable dosages of PTFE. The coated substrates' superhydrophobicity was evaluated by measuring the water contact angle. After that, a statistical analysis was conducted to determine the significant parameters affecting the superhydrophobicity of the coated asphalt concrete substrates. Based on the findings obtained from the statistical analysis, the PTFE was sprayed over the surface of asphalt concrete. Finally, the skid resistance was obtained by measuring the BPN over the coated and uncoated substrates. The findings of this study are discussed to provide some guidance on actual implementation of the use of superhydrophobic coated asphalt concrete for ice- and snow-free flexible pavement applications. We hope that the obtained results will help mitigate the problems associated with ice/snow formation on the surface of roadways and paved areas of airfields after implementing and testing these materials at larger scales in the field.

2. MATERIALS AND METHODOLOGY

In order to investigate the effect of different variables on the superhydrophobicity of the nano-coated asphalt concrete substrates, a statistical design was developed and performed prior to the start of experiments. The selected variables were the spray times (3, 6, 9 and 12 seconds) and dosages (10, 20, 30 and 40%) of PTFE. As the result of statistical design, 28 disk-shaped asphalt concrete substrates were prepared. 16 substrates were used for measuring the contact angles each of which were divided to four quarters for the sake of obtaining replicates. Three replicates were used for coating, i.e., forty-eight (16×3) samples were coated. Each coated sample's superhydrophobicity was evaluated through measuring the water contact angle. The measured contact angles were statistically analyzed, and based on the obtained results, the uncut surface of 12 disk-shaped asphalt concrete samples were coated at the significant spray time and the four dosages of PTFE.

2.1. Preparation of asphalt concrete substrates

Asphalt concrete samples which were prepared at laboratory for this study consisted of limestone - having a gradation consistent with Superpave mix design and Federal Aviation Administration’s (FAA) advisory circular [19], and bitumen at optimum content.

Using a gyratory compactor, mixtures were compacted in a cylindrical mold, with a diameter of 100 mm and a height of 150 mm, to achieve 4% air void in the Superpave gyratory compactor. After the compaction, a table diamond saw was used for making 7 cross sectional cuts through each cylindrical asphalt concrete specimen to obtain six 10 mm-thick substrates. 4 number of disk-shaped specimens were obtained from the core of each cylindrical sample. Each disk-shaped specimen was cut to four quarters. Figure 1 illustrates the preparation of substrates. Hereinafter, quarter disk-shaped asphalt concrete specimen is referred to as asphalt concrete specimen/substrate. In order to measure the resistance against sliding, the two remaining cuts were made near top and bottom of the cylindrical samples so that the skid resistance could be measured over the surface texture of asphalt concrete.

Figure 1: Preparation of asphalt concrete substrates at the laboratory

2.2. Coating the asphalt concrete substrates

There are different methods including layer by layer (LBL), wax solidification, lithography, polymer conformation, vapor deposition, sublimation, plasma technique and others for synthesizing the superhydrophobic surfaces [20]. Because of asphalt concrete’s non-planar surface, the specimens used in this study were coated using the LBL method [20]. In order to achieve LBL coating, at first, a two-part epoxy resin dissolved in xylene (first layer) was first sprayed on the top surface of each asphalt concrete specimen. After that, the PTFE dispersed in acetone (second layer) was sprayed over the epoxy resin. PTFE was added to acetone based on different weight percentages of epoxy resin.

The epoxy (EP 1224), acquired from ResinLab, consisted of two parts: part A - a polymer resin - and part B - a curing agent. For coating each asphalt concrete specimen, 10 mL of part A, 5 mL of part B and 15 mL of xylene were introduced to a beaker. The obtained batch was magnetically stirred for 5 minutes at 500 rpm at ambient temperature. Hereinafter, this batch is referred to as epoxy. After the stirring time was over, the epoxy was immediately introduced to a spray gun (Figure 2) allocated for epoxy, and was sprayed over an asphalt concrete substrate for three seconds at once. In order to eliminate the hardening effect of the epoxy over time, the remaining amount in the paint cup was disposed; for each spray deposition, one fresh new batch was prepared

So far, the feasibility of using PTFE as an icephobic material has been investigated on the outdoor structures - like ground wires, phase conductors of overhead power lines, aircraft wings and fuselage, telecommunication antennas and conductors [21–23]. Note that this research mostly highlights the application of superhydrophobic materials on asphalt concrete. Zynol® MP 1300 PTFE obtained from DuPont was dispersed in acetone at different dosages; the dosages were calculated based on the percent weight (10, 20, 30 and 40%) of the two-part epoxy. PTFE, at each dosage, was introduced to acetone to obtain a 50 mL mixture. The mixture was magnetically stirred for 15 minutes at 500 rpm at ambient temperature; then it was immediately introduced to a spray gun specifically used for spraying PTFE/acetone mixture. The mixtures of acetone and PTFE were sprayed on the asphalt concrete substrates at different time durations of 3, 6, 9 and 12 seconds (Figure 2). It is worth mentioning that, two separate spray guns for spraying PTFE and epoxy were used to prevent the contamination of the spray materials with one another. In order to measure the skid resistance over the surface of cylindrical specimens, they were coated in the same way. However, the coating was performed at just one selected spray time and different dosages of PTFE.

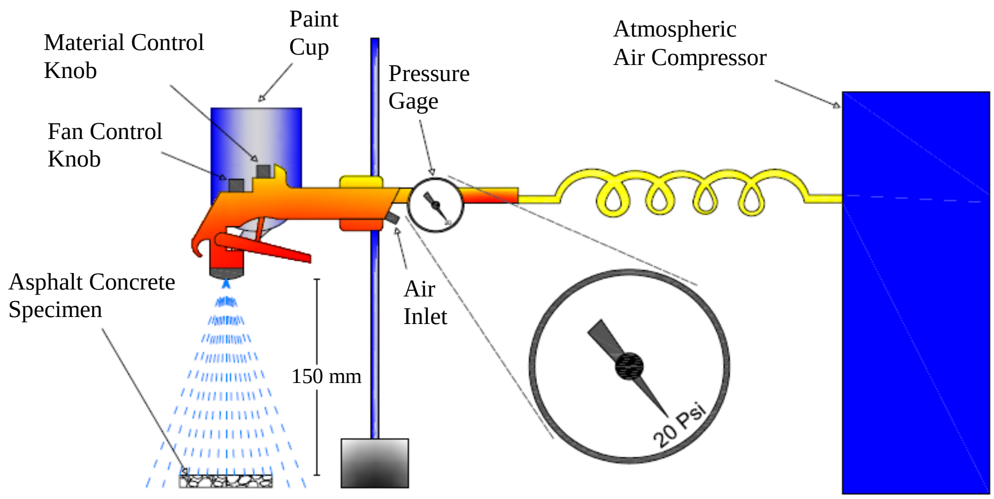

Figure 2: Spray gun set up for spraying the epoxy and the PTFE

Note that, Figure 3 depicts two different scenarios that might happen during the PTFE and epoxy deposition. If the dosage of PTFE is low and the spraying time is too short, either the amount of PTFE nanoparticles sticking to the surface will be very small or the PTFE nanoparticles will sink into the epoxy. When the spraying time is too long and the dosage of the PTFE particles is high, some nanoparticles will accumulate on the surface without binding to the substrate, and the nanoparticle deposition will be uneconomical.

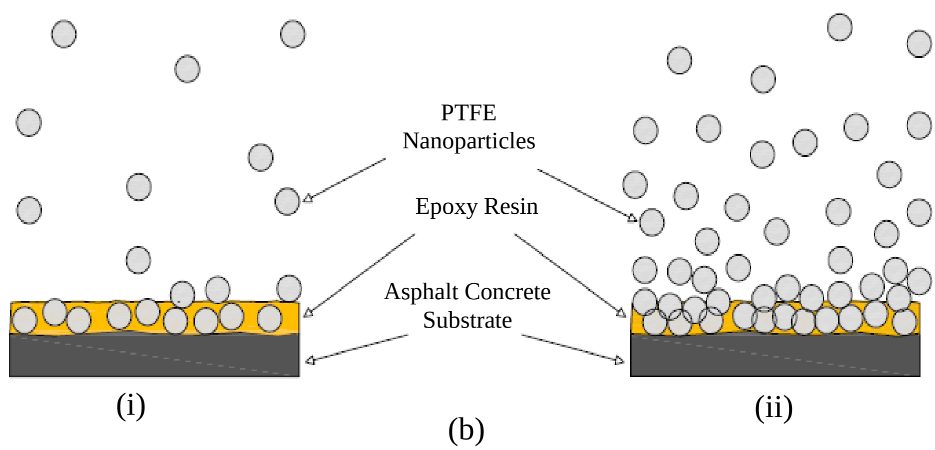

Figure 3: Deposition of nanoparticles when the amount of PTFE is (i) low and (ii) high

2.3. Magnifying and capturing the water droplets

In order to measure the contact angle, 4 µL water droplets were deposited on three spots over the surface of each specimen. The droplets were big enough to enable the deposition, and were small enough to decrease the effect of gravity on their shapes. After the deposition, the droplets were allowed to relax for 30s to reach equilibrium [24]; then, they were magnified and imaged by a high-magnification Sony camera. Figure 4 illustrates the test set-up used for magnifying and capturing the water droplets to measure the water contact angles. The test was performed at the controlled environmental conditions of 25° C and relative humidity of 60%.

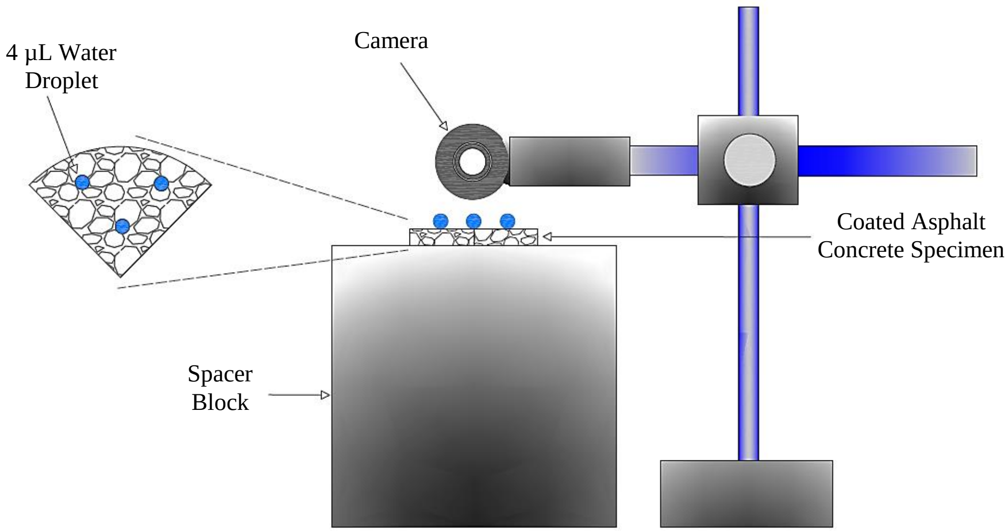

Figure 4: Set-up used for measuring the contact angles

2.4. Data collection for measuring the skid resistance

There are different approaches for measuring the skid resistance like using the locked-wheel equipment, continuous friction measuring device, British pendulum tester, etc. For example, in the current state of practice - according to ASTM E274 - the skid resistance of flexible pavements is usually measured at 65 km/h using the locked-wheel method [25]. According to FAA's advisory circular - which is another guideline among the available standards, the skid resistance of asphalt concrete can be measured in the field at either 65 or 95 km/h using a continuous friction measuring equipment (CFME) [19]. However, unlike the two aforementioned methods, British pendulum test specified in ASTM E303, can be used both in the field and at the laboratory for measuring the skid resistance over the surface of asphalt concrete.

This research mostly highlights using British pendulum tester for measuring the skid resistance on the surface of nano-coated asphalt concrete at laboratory (Figure 5). The skid resistance of the coated and uncoated samples were investigated by obtaining the BPNs according to the ASTM E303. However, the sliding length of the pendulum was modified and decreased due to the small diameter (100 mm) of the cylindrical asphalt concrete samples. In order to make sure that the obtained BPN values were correct and precise, each of the specimens were fixed beneath the British pendulum tester by using a strong two-sided tape. Before performing the measurements, the surfaces were made wet using a water sprayer. Then, four measurements were performed on each of the cylindrical samples – each having three replicates - before and after the coating, and the BPN values were recorded. It is worth noting that, the measurements on each sample (before and after coating) were all performed in same direction. In this way, the chance of any possible induced variability in the obtained BPN values was eliminated - the morphology of the surface texture at different directions is not the same.

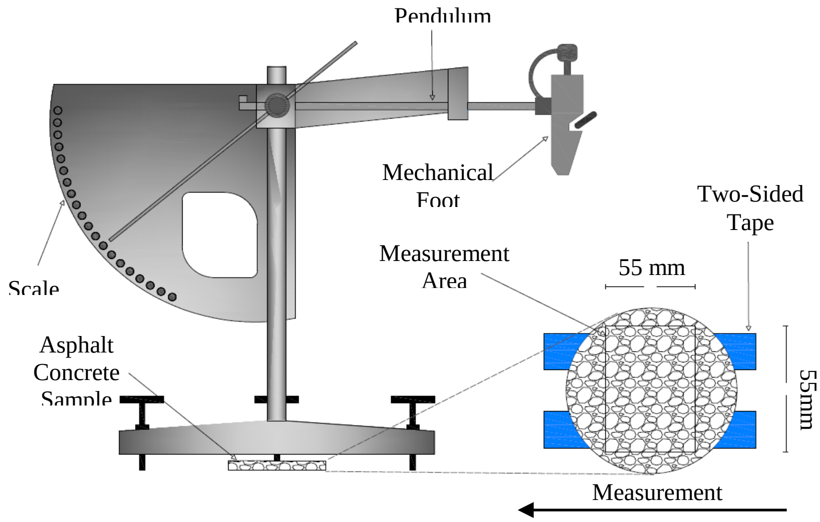

Figure 5: Schematic of British pendulum tester

3. RESULTS AND DISCUSSION

3.1. Contact angle measurements

Using the sessile-drop and tangent line method - among the available methods [20] , the static contact angles of the three deposited water droplets were measured with an on-screen protractor (Figure 6). Then the three measured values were averaged for each specimen. It is worth noting that, each specimen had three replicates on each of which three water contact angle measurements was performed. The water contact angle value is an indication of surface hydrophobicity. It is the angle measured between the tangent lines drawn on solid-liquid (SL) and liquid-gas (LG) interfaces. The higher the measured water contact angle the higher the hydrophobicity. If the measured water contact angle is equal to or higher than 150º, the surface will be superhydrophobic. If the measured water contact angle is equal to or higher than 90 º - but still lower than 150º-, the surface will be hydrophobic. The water contact angles lower than 90 º, are representative of the surfaces which are hydrophilic.

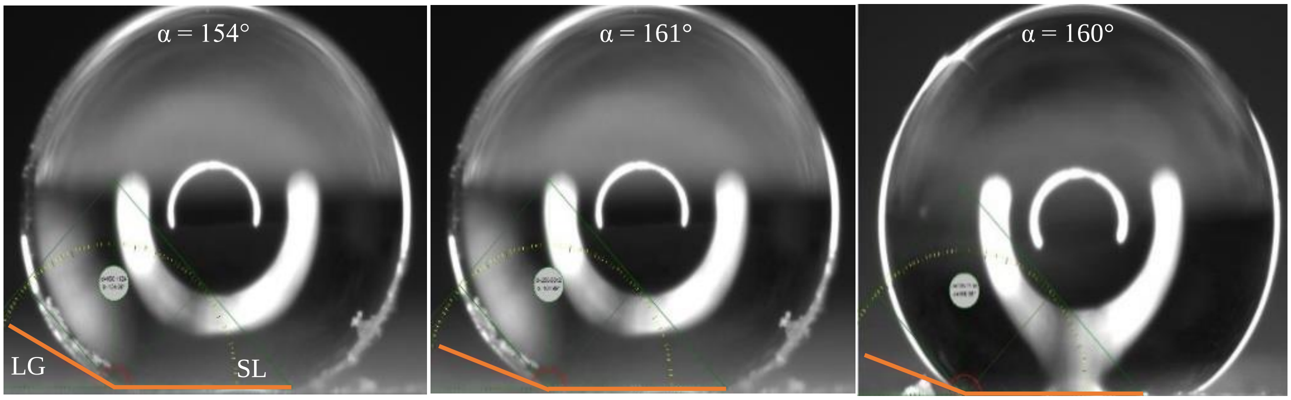

Figure 6: An example of water contact angle measurement for three droplets deposited on one replicate

The averaged values of measured water contact angles for each spraying time and PTFE dosage are presented in Table 1.

Table 1: Measured contact angles (degrees)

Spray Time (s)	PTFE (%)							
	10		20		30		40	
	Ave.[1]	SE[2]	Ave.	SE	Ave.	SE	Ave.	SE
3	125	8.3	152	5.4	155	2.6	150	4.8
6	156	2.9	157	3.1	156	2.5	155	1.7
9	161	3.2	154	5.8	165	2.5	158	2.1
12	156	9.0	156	3.9	161	1.6	166	1.5

Note: [1]Ave stands for the average and [2]SE stands for the standard error.

A statistical analysis was conducted on forty eight averaged water contact angles (See Table 1); based on the analysis, the spray time and the percentage of PTFE – in order of priority - became the significant factors.

It is important to note that, in Table 1, the superhydrophobicity is achieved at the 6-second spray time for all of the different percentages of PTFE. Moreover, increasing the spray time from 3 to 6 seconds resulted in a proportional increase in the hydrophobicity. Increasing the spray time after 6 seconds does not considerably increase the superhydrophobicity for different percentages of PTFE except for 40%.

The highest contact angle of 166° is achieved at the spray time of 12 seconds and the PTFE percent of 40. The reason for having such high contact angle can be attributed to the well and thorough distribution of nanoparticles over the sample. However, it should be kept in mind that, for the purpose of ice/snow removal from the pavement/runway, it is enough to achieve 150-degree contact angles [11]. In other words, the goal for curbing the ice or snow formation is achieved at the water contact angle of 150°. Adding to the amount of PTFE by either increasing the spray time more than 6 seconds or the dosage of PTFE more than 20%, is not an economical approach.

The reason for obtaining low hydrophobicity (i.e., the lowest contact angle of 125°) at 3-second spray time and 10% of PTFE can be attributed to the way that PTFE particles are deposited on the epoxy layer. When the amount of PTFE particles are low, they sink into the adhesive layer and the accumulation of nanoparticles on the sunken ones is not enough to cover the whole surface of the specimen in a uniform manner.

Based on the results of statistical analysis, the disk-shaped asphalt concrete specimens were coated at the 6-second spray time with the four dosages of PTFE. In order to depict the behavior of water droplets, a portion of a cylindrical asphalt concrete specimen was coated with PTFE using the LBL method (Figure 7). Note that in Figure 7, the water droplets form a spherical shape on the coated side meaning that they do not tend to wet the surface.

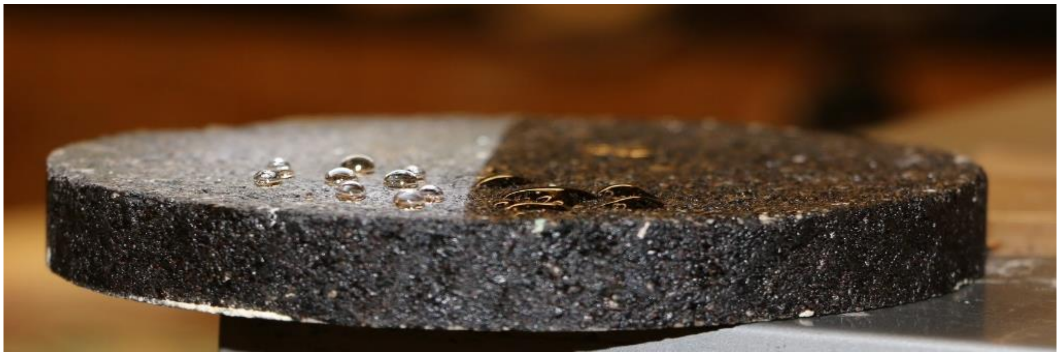

Figure 7: The behavior of water droplet on the coated (left) and uncoated (right) cylindrical asphalt concrete specimens

3.2. Skid resistance measurements

Four measurements were performed on each replicate. In total twelve BPN measurements were obtained from each specimen. Then, the measured BPN values were averaged for each specimen. Figure 8 represents the averaged values of BPN at different dosages of PTFE and the spray time of 6 seconds. Note that increasing the PTFE percent from 10% to 30 % considerably increases the skid resistance. However, further increase of PTFE dosage results in obtaining less skid resistant surfaces. The reason for this behavior can be attributed to the saturated amount of PTFE present on the surface of the asphalt concrete. The excessive amount of these particles are not able to bind to the epoxy. As a result, when the mechanical foot slides over the surface, it can easily wipe the free PTFE particles off the surface causing the British pendulum tester show lower BPNs.

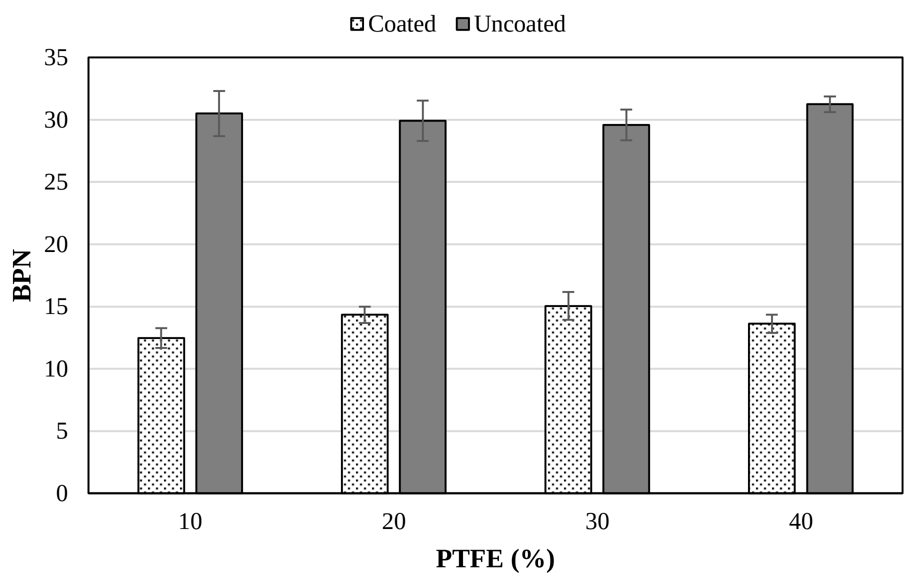

Figure 8: Averaged BPN values

The 10% of PTFE dosage provided the lowest skid resistance. The reason for this behavior can be attributed to presence of spots on epoxy not covered with PTFE. At this low dosage of PTFE, nano-particles may cover the surface, but after that they sink into the epoxy. In order to overcome this problem, the dosage should be increased so that the PTFE particles can agglomerate on top of each other and then cover the surface.
Lower BPN values obtained from the PTFE coated specimens are indications of making improvements in further studies, such that the skid resistances measured on coated and uncoated asphalt concrete become comparable. Additional investigation is needed for implementing the use of superhydrophobic coatings in actual snow and ice removal strategies for the flexible pavement systems.

4. CONCLUSIONS

In this study, the layer by layer (LBL) method was employed to create superhydrophobic coatings. A statistical design based experimental test program was developed and conducted to evaluate the effect of different test variables including spray times and dosage rates of PTFE on the superhydrophobicity of the coated asphalt concrete. Based on the results obtained from the statistical analysis, cylindrical asphalt concrete samples representing the texture of flexible pavements were coated with PTFE. The skid resistance of the coated samples were evaluated with a modified British pendulum tester. The major conclusions drawn from test procedures and results are summarized below:

- Using the LBL method for spray depositing the PTFE particles seems to be a promising method for achieving ice-repellent surfaces and mitigating the problems associated with ice accretion or snow accumulation on the roadways or airfield areas.

- Increasing the spray duration from 3 seconds to 6 seconds resulted in achieving water contact angles higher than 150°. The super water-repellency did not uniformly increase for all of the specimens after 6 seconds. Increasing the amount of PTFE, up to a certain level, in nano-coating of asphalt concrete also increases the ice/snow repellency. After that level, adding to the deposition amount of PTFE is uneconomical, and does not increase the superhydrophobicity in a considerable manner.
- The skid resistance of the cylindrical samples coated at the selected spray time of 6 seconds, was enhanced by increasing the dosage of PTFE up to 30%. However, application of PTFE by using LBL method decreases the skid resistance compared with the uncoated asphalt concrete.

5. RECOMMENDATIONS

Further investigations are recommended to prevent on the reduction of skid resistance found in this study using LBL method and British pendulum test. Other deposition techniques like composite coating can be alternative to LBL method. Moreover, cylindrical specimens with bigger diameters should be tested so that the pendulum's mechanical foot can slide over a larger area. Instead of using PTFE for making the surface of asphalt concrete ice-repellent, it is possible to combine the PTFE with other materials like polymers or use other nano-particles with hydrophobic characteristics to enhance the skid resistance with maintaining the superhydrophobicity.

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