Influence of Deicing Salts on the Water-Repellency of Portland Cement Concrete Coated with Polytetrafluoroethylene and Polyetheretherketone

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ABSTRACT

Sustainable super water/ice-repellent pavements are gaining attention as a smart solution for mitigating problems associated with winter pavement maintenance of roadways and airfields. Such smart pavements can facilitate surface drainage and prevent or curb ice formation or snow accumulation. While a conventional method for melting ice and snow is the use of deicing chemicals, such materials can transfer to the surface of nanotechnology-based pavements and influence their water/ice-repellency by changing the chemistry of water or ice. This study focused on characterizing the degree of hydrophobicity of Portland cement concrete (PCC) nano-coated with polytetrafluoroethylene/polyetheretherketone (PTFE/PEEK). A layer-by-layer (LBL) spray deposition technique was used for spraying the binding agent and water-repellent materials. The liquid-repellency was characterized by measuring the static liquid contact angles (LCAs) and calculating the works of adhesion (WAs). The liquid types used included distilled water and two types of deicing chemicals prepared by dissolving salts in distilled water. Data analysis results revealed that salt contamination improves the water-repellency of nano-coated surfaces.

INTRODUCTION

Winter pavement maintenance of roadways and paved areas of airfields has always been a challenging task for highway agencies and airport authorities. To some extent, conventional methods like the use of deicing chemicals and deployment of snow-plowing equipment have remedied problems associated with snow accumulation and ice formation. Needless to say, such deicing chemicals can have detrimental effects on Portland cement concrete (PCC) and the use of snow-plowing equipment is costly and time-consuming. Due to such conventional methods' deficiencies, emerging technologies such as heated pavement systems and nano-technology-based super water/ice-repellent pavement surfaces have drawn the attention of researchers from all around the globe (Abdualla et al. 2016; Sassani et al. 2017; Nascimento et al. 2003).

Superhydrophobicity (super water-repellency), which also typically leads to ice-repellency (Cao et al. 2009), is defined as the ability of a surface to keep water away without allowing it to wet the surface (Zhang et al. 2008). There are many surfaces in nature with this fascinating capability, e.g., lotus leaves. The slightest tilt angle in a lotus leaf causes the water droplets to roll off its surface – under the influence of gravity - while trapping and carrying dirt particles. The water-repellency and self-cleaning properties of the lotus leaf are referred to as the "lotus effect" (Von Baeyer 2000). The degree of water-repellency of a surface can be quantified through water contact angle (WCA) - or liquid contact angle (LCA) - measurement and the calculation of work of adhesion (WA) (Arabzadeh et al. 2016a). LCAs greater than 150 ° are indicative of superhydrophobicity, and lower WA means higher tendency of a surface to repel liquids that in the context of this study are aqueous solutions.

According to reported literature, a few biomimetic approaches have been successfully attempted for transferring the "lotus effect" to PCC surfaces (Flores-Vivian et al. 2013; Horgnies and Chen 2014; Arabzadeh et al. 2017) and asphalt concrete surfaces (Arabzadeh et al. 2016b; Nascimento et al. 2003) to make them water/ice-repellent. However, the water-repellency of nanotechnology-based hydrophobic pavements in the presence of contaminants like deicing chemicals has not been considered. Deicers applied on conventional surfaces can be transferred to water-repellent surfaces by surface runoff or wind and subsequently influence their hydrophobicity.

A hydrophilic surface like that of PCC can become superhydrophobic if two rules are followed (Onda et al. 1996). First, a hierarchical roughness - a combination of micro and nano roughness - must be produced on the concrete surface. Second, the surface chemistry should be transformed using low surface energy materials. There are various methods for synthesizing super water-repellent surfaces (Zhang et al. 2008) like the layer-by-layer (LBL) spray deposition method that can help achieve the desired roughness (Arabzadeh et al. 2016a). Utilizing this method for spray deposition of low surface energy materials like Polytetrafluoroethylene (PTFE) and polyetheretherketone (PEEK) can help achieve superhydrophobicity (Ourahmoune et al. 2011; Zhang and Han, 2004; Ceylan et al. 2016).

In this study, the surfaces of PCC substrates were nano-coated using a layer-by-layer (LBL) spray deposition technique. PTFE and PEEK were the water-repellent materials used. Three types of liquids were used for evaluating the water-repellency;

two were a sodium chloride solution and a calcium chloride dihydrate solution, and the other was distilled water used for control purposes. The liquid-repellency of the surfaces were evaluated by measuring the LCAs and the WAs, with results that revealed that presence of deicing chemicals enhances the water-repellency of the surface of nano-coated Portland cement concrete.

MATERIALS AND METHODOLOGY

Four quarter-sized disk-shaped PCC substrates were prepared and then coated with PTFE/PEEK. To investigate the effects of different deicing chemicals on the superhydrophobicity of nano-coated Portland cement concrete substrates, two different solutions – each at 20% concentration - were prepared prior to the start of the experiments. Each coated sample's hydrophobicity was evaluated by measuring its liquid contact angle (LCA) and its work of adhesion (WA).

Preparation of Portland cement concrete (PCC) substrates. The concrete samples were prepared following the Iowa DOT mix design (Materials I.M. 529) guideline and the FAA advisory circular (FAA 2014). A type I/II cement manufactured by Holcim was utilized and the water-to-cement ratio was maintained at 0.4. The selected coarse aggregate was limestone with a nominal maximum aggregate size of 25 mm. The utilized fine aggregate was river sand.

Prepared fresh concrete was cast into cylindrical molds with diameters of 100 mm and heights of 200 mm. The cylindrical specimens were cured for twenty-eight days at 23ºC at a relative humidity of 100%. After the curing period, the specimens were cut with a diamond saw so that a total of 8 disk-shaped substrates with 10 mm thickness could be obtained from the core of each cylindrical specimen. Cutting the substrates from the center guaranteed the uniformity and evenness of their surfaces. It is worth noting that, to increase accuracy of results, only the highest quality disk-shaped substrate was selected and the rest were discarded. In this way, visual observation ensured that the selected surface had the minimum amount of pores. The selected disk-shaped substrate was further cut into quarters to increase the number of replicates (Figure 1).

Figure 1. Preparation of PCC substrates in the laboratory.

Coating the Portland cement concrete substrates. Because of PCC's non-planar surface, the specimens used in this study were coated using the LBL method (Zhang et al. 2008) in which a two-part epoxy resin dissolved in xylene was first sprayed on the top surface of each PCC substrate, forming the first layer. Then PTFE and PEEK dispersed in acetone were immediately spray deposited, forming the second layer. The reason for selecting PEEK stems from the fact that this material provides reasonable wear and skid resistance (Vail et al. 2011; Arabzadeh et al. 2017).

The epoxy (EP 1224), acquired from ResinLab, was comprised of two parts: part A (a polymer resin) and part B (a curing agent). For coating each PCC substrate, 20 mL of part A, 10 mL of part B, and 30 mL of xylene were placed in a beaker, and the mixture obtained was magnetically stirred for 10 minutes at 500 rpm at ambient temperature. Hereinafter, this mixture will be referred to as a binder. After the stirring process, the binder was immediately put into a spray gun allocated for binder deposition and sprayed over each PCC substrate for three seconds (Figure 2). To eliminate the hardening effect of the binder over time, the remaining amount in the paint cup was discarded. For each spray deposition, a fresh new batch was prepared

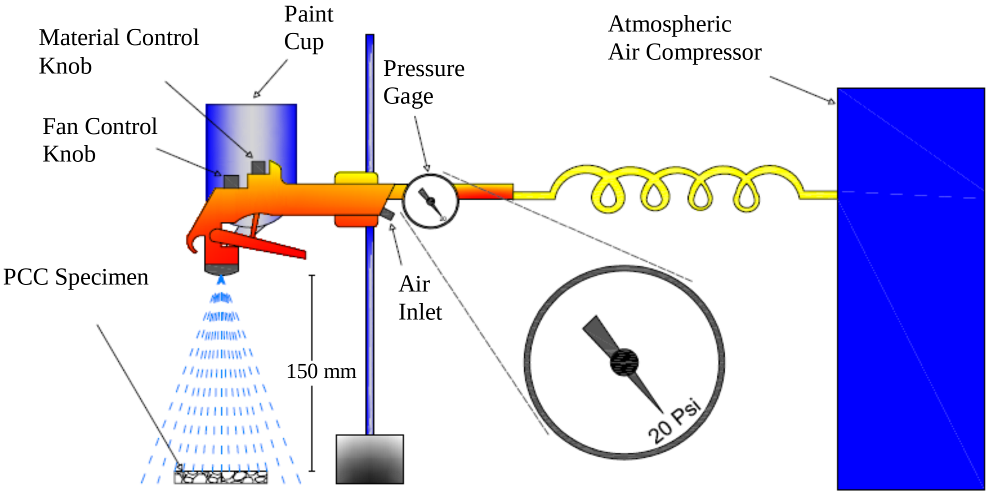

Figure 2. Spray gun set-up for spraying the binder and suspension.

Zynol® MP 1300 PTFE - obtained from DuPont - and Vestakeep PEEK - acquired from HT Polymers - were mixed and dispersed in acetone. First, 9 grams of PTFE and 1 gram of PEEK were added acetone to obtain a 60 mL mixture. The mixture was magnetically stirred for 15 minutes at 500 rpm at ambient temperature to obtain a uniform suspension; the mixture was immediately introduced into a spray gun specifically used for spraying the suspension (see Figure 2) and sprayed for 6 seconds on each PCC substrate coated with the fresh binder. It should be mentioned that separate spray guns were used for spraying the PTFE and the epoxy so that the sprayed materials would not be mixed or contaminated.

Preparation of the deicing solutions. Following the guideline provided by FHWA-RD-202 (Ketcham et al. 1996), the solutions of two most commonly used deicing chemicals, sodium chloride (NaCl) and calcium chloride dihydrate ($CaCl_2H_4O_2$), were prepared at the relatively high concentration of 20% (Wåhlin and Klein-Paste 2016). It is worth noting that calcium chloride is mostly found in a hydrated form having the generic formula $CaCl_2 (H_2O)_x$, where x can be 1, 2, 4, or 6. Any of these compounds - like the calcium chloride dihydrate or $CaCl_2H_4O_2$ - can be used for deicing purposes; while the anhydrous calcium chloride or $CaCl_2$ is mainly used as a desiccant (Kemp and Keegan 2012).

To prepare the sodium chloride solution, 20.40 gr of NaCl was added to 100 mL of distilled water to achieve a liquid with density of 1.15 gr/m^3. Then, 34.40 gr of calcium chloride dihydrate was added to 100 mL of distilled water to achieve a liquid with density of 1.19 gr/m^3. Each mixture was magnetically stirred for 10 minutes at 400 rpm. After preparation of the solutions, they were allowed to rest for at least a day to reach equilibrium and become stabilized at room temperature. In this way, it was ensured that heat generation due to reaction between the salts and the distilled water would not affect the accuracy of LCA measurement results.

Magnifying and imaging the liquid droplets. To measure the liquid contact angles (LCAs) of the distilled water and the two deicing solutions, 4 µL liquid droplets were deposited at four spots over the surface of each replicate, i.e., 16 liquid droplets were deposited for each liquid type. The droplets were large enough to facilitate the deposition and small enough to nearly eliminate the effects of gravity on their shapes. After deposition, the droplets were allowed to relax for 30s in order to allow them to reach equilibrium (Kwok and Neumann 1999), then they were immediately magnified and imaged by a high-magnification Sony camera. Figure 3 illustrates the test set-up used for magnifying and imaging the liquid droplets to measure the LCAs. The test was performed at room temperature and at a relative humidity of 67%.

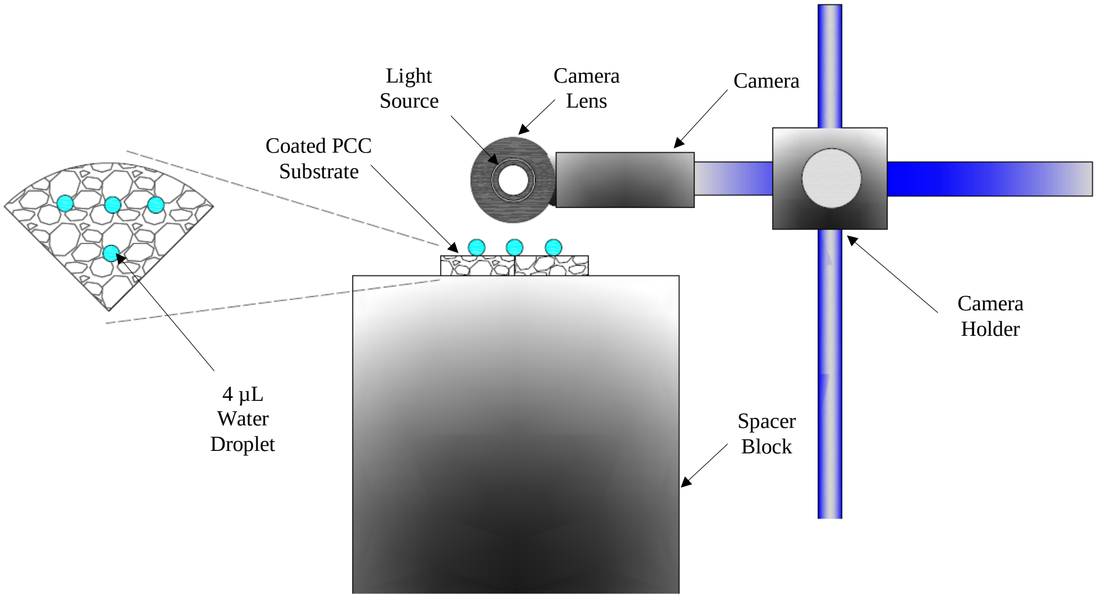

Figure 3. Set-up used for measuring the liquid contact angles.

RESULTS AND DISCUSSION

Liquid contact angle measurements. Utilizing the B-spline snake (B-snake) method (Stalder et al. 2006), the static liquid contact angles (LCAs) of the sixteen deposited liquid droplets (one for each liquid type) were measured in the ImageJ ® environment (Figure 4). This software measures two liquid contact angles (LCAs) at the left and right sides of each liquid droplet, and the reported LCA is the arithmetic mean of the two measured values.

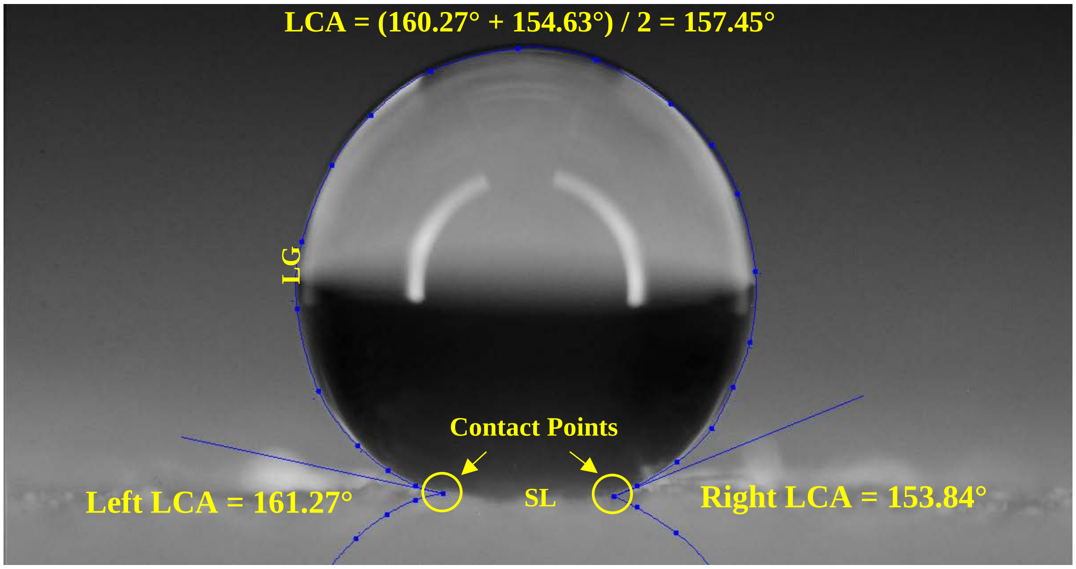

Figure 4. An example of water contact angle measurement in ImageJ ® environment using the drop analysis plugin.

The measured LCA is an indication of surface liquid-repellency. Since in this study the liquids are solutions composed of distilled water with dissolved salts, the liquid contact angles can be indicative of water-repellency.

Contact angle is the value measured between the solid-liquid (SL) and liquid-gas (LG) interfaces at the contact points where tangents are drawn. The higher the measured LCA, the higher the water-repellency of the surface. If the contact angle is lower than 30º, the surface is considered hydrophilic (Muzenski et al. 2014). If the contact angle is equal to or greater than 90º, but still lower than or equal to 120 º, the surface is considered hydrophobic. When the contact angle is between 120 º and 150 º the surface is considered overhydrophobic (Muzenski et al. 2014). A measured LCA equal to or greater than 150 º is an indication of superhydrophobicity (Nosonovsky 2007).

All of the measured LCAs for distilled water, the sodium chloride solution, and the calcium chloride dihydrate solution are presented in Table 1.

Table 1. The Measured LCAs (Degrees).

Droplet No.	Distilled water	NaCl Solution	$CaCl_2H_4O_2$ solution
1	151.72	120.59	156.91
2	155.75	147.61	142.69
3	138.30	157.45	147.68
4	155.91	153.42	153.61
5	151.94	159.08	155.52
6	152.83	152.21	147.10
7	152.23	154.39	145.88
8	153.92	154.49	150.24
9	154.13	154.18	148.32
10	154.05	157.45	154.51
11	123.38	159.84	152.96
12	150.84	148.53	154.33
13	134.93	152.58	153.12
14	157.86	148.57	164.11
15	154.98	155.69	156.73
16	147.74	152.11	154.10
Average	149.40	151.76	152.36
Standard Error	2.32	2.27	1.30

The selected spray duration of 6 seconds results in obtaining an overhydrophobic surface ($120^\circ <$ average LCA $= 149.4^\circ < 150^\circ$) when the PCC surface is not contaminated by deicing chemicals. Addition of sodium chloride or calcium chloride dihydrate to the distilled water improves the degree of water-repellency. The LCAs reveal that the surfaces become superhydrophobic when contaminated by deicing chemicals. The highest LCAs are achieved for the calcium chloride dihydrate solution. Calcium chloride can cause the most severe damage in Portland cement concrete by producing pressure (through osmosis) and crystallization or corrosion (Wang et al. 2006). Presence of water-repellent materials can inhibit the penetration of detrimental chemicals from the surface, resulting in reduction of damage related to corrosion and salt scaling; the chemicals can still penetrate the concrete from the sides and the bottom of the slabs used in rigid pavements.

The reason for having low contact angles like 123.38 ° or 120.59 ° can be attributed to the presence of pores on the substrate surface. Even though the substrate surfaces were thoroughly inspected, having a pore-free surface on PCC is inevitable. Pores are voids induced because of entrained or entrapped air, and they also can be formed during the cement hydration process.

Measuring the work of adhesion. In this study, the work of adhesion (WA) can be defined as the work that must be done to separate two neighboring phases of a liquid-solid interface (Packham 1996). Similarly to the liquid contact angle, the WA can reveal the water-repellency degree of any nano-coated surface (Arabzadeh et al. 2016a;

Nascimento et al. 2003). The work of adhesion (W_A) can be calculated using the Young-Dupré equation:

$$W_A = \gamma_{LV}(1 + cos\theta)$$

where θ is the liquid contact angle and γ_{LV} is the surface tension of water, 72.8 mN/m.

Figure 5 represents the WAs calculated and averaged for each liquid type. As expected, the calcium chloride dihydrate solution had the lowest work of adhesion, followed by the sodium chloride solution and then the distilled water. A lower WA, produces a greater tendency for the surface to repel water. If calcium chloride dihydrate and sodium chloride are the contaminants, they can improve the water-repellency of nano-coated rigid pavements.

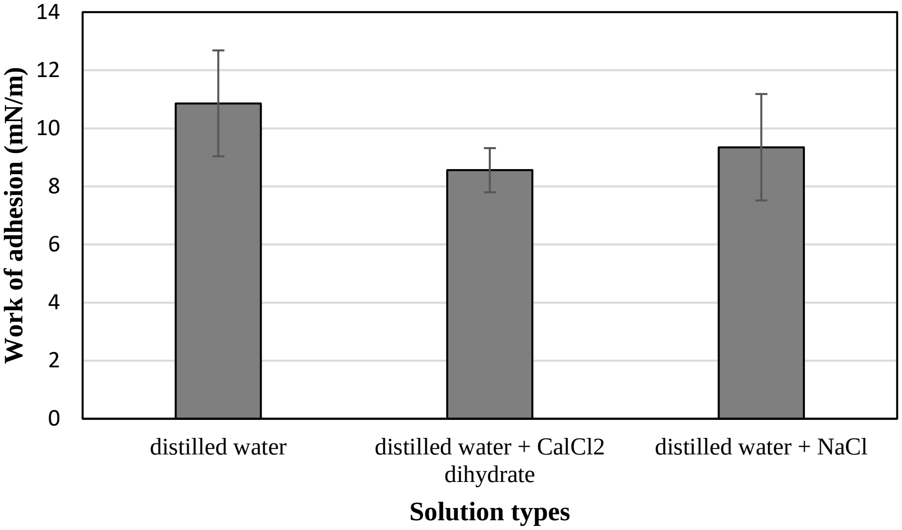

Figure 5. Averaged measured works of adhesion.

CONCLUSIONS AND RECOMMENDATIONS

The goal of this study was to evaluate the hydrophobicity of nano-coated Portland cement concrete (PCC) in the presence of contaminants like deicing chemicals. To this end, layer-by-layer (LBL) spray deposition techniques for coating the Portland cement concrete (PCC) substrates with PTFE/PEEK were utilized. Three types of liquids were used for evaluating water repellency. Two of these liquid types were sodium chloride solution and calcium chloride dihydrate solution and the third was distilled water used for control purposes. The liquid repellency of the surfaces were evaluated by measuring liquid contact angles (LCAs) and works of adhesion (WAs).

The LCA measurement results and the calculated WAs revealed that contaminants like sodium chloride and calcium chloride dihydrate enhance the hydrophobicity of nano-coated PCC. The LCAs measured on droplets of distilled water proved the occurrence of overhydrophobicity of the surfaces, while the LCAs measured on the liquid droplets containing sodium chloride or calcium chloride dihydrate proved the occurrence of superhydrophobicity of the surfaces, especially when the measurements were performed on liquid droplets containing calcium chloride dihydrate. Based on this preliminary study, it can be stated that there should be no concern regarding the presence of sodium chloride and calcium chloride dihydrate on nano-coated rigid pavements, i.e., these surfaces are self-cleaning and will help wash deicing salts away. However, the durability of the PTFE/PEEK coating against long exposures to these two types of deicing chemicals should be investigated in future studies. There are also other types of candidate coatings that should be tested by studying their performance in presence of deicing chemicals. Moreover, the hydrophobicity of coated PCC should be evaluated when other types of substances such as oil, gasoline, jet fuels, etc. contaminate the paved surfaces.

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