C-2-5 Superhydrophobic self-cleaning cool concrete pavement coating and its potential to mitigate the urban heat island effect

Zhuo Yang
School of Civil Engineering, North China University of Technology, Beijing 100144, China.

Jie Qin
Technical Center, China State Construction Engineering Co., Ltd., Beijing 101300, China.

Yanwen Li
Technical Center, China State Construction Engineering Co., Ltd., Beijing 101300, China.

Tao Zhang
Technical Center, China State Construction Engineering Co., Ltd., Beijing 101300, China.

Jian Qu
Technical Center, China State Construction Engineering Co., Ltd., Beijing 101300, China.

Weidong Zhang
Technical Center, China State Construction Engineering Co., Ltd., Beijing 101300, China, zwdpt@sohu.com

ABSTRACT: A method of fabricating an industrially producible, broadly applicable, and easily repairable super-water-repellent self-cleaning solar reflective concrete pavement coating from commercially available cost-effective materials for the mitigation of the urban heat island effect. Grinding of the hydrophobic coating with emery papers generates appropriately sized micro-grooves and exposes micro-particles on the coating surface, thereby imparting the coating surface with super-water-repellency and self-cleaning capacity. When applied to original and outdoor-exposed concrete pavements, the solar reflective concrete pavement coating with a metameric color match to the desired concrete-color is estimated to yield cooling effects of 15.1 and 24.0 °C, respectively, on a typical hot summer day. After 240 h of artificial accelerated weathering, the spectral and solar reflectances of the solar reflective pavement coating are attenuated and the super-water-repellency of the coating is lost as a result of the degradation of the low-surface-free-energy materials on the coating surface, and the damage to surface structures caused by periodic spraying with water. The diminished super-water-repellency and self-cleaning properties of the weathered coating surface are fully re-established after the weathered coating surface is ground using emery papers with appropriate grit numbers.

KEY-WORDS: Superhydrophobic, self-cleaning, solar reflective, pavement coating, cooling effect, heat island effect, artificial accelerated weathering

INTRODUCTION

Concrete pavements and asphalt concrete pavements (AC) cover a significant geographical area of urban surfaces [1-6]. Conventional concrete and AC pavements have a typical initial solar reflectance of 0.45 and 0.04, respectively [2,4] with surface temperatures that range from 48 to 67 °C in summer [2]. As a consequence, pavements make a significant contribution to the urban heat island effect (UHIE) [6,7]. The use of solar reflective coatings to increase the solar reflectance of pavements represents a well-established and effective mitigation measure for combatting UHIE [6]. Increasing the solar reflectance of a pavement reduces its surface temperature, keeps it cool, decreases the convection of heat from the pavement to air, and thereby also lowers the ambient air temperature [1, 2].Thus, it is necessary to use near-infrared (NIR) reflective materials with a low spectral reflectance in the visible (VIS) regime [8]. A recent study reported that the solar reflectance of solar reflective AC pavements decreased from 0.33 to 0.17, mainly as a result of hydrophilic compounds emitted from motor vehicles and the deposits from vehicle tires, it is also can be restored to nearly original levels after washing with water [8]. These observations imply that self-cleaning solar reflective pavement coatings may solve effectively and economically the attenuation challenge associated with solar reflectance.

Superhydrophobic coatings with a minimum water-contact angle (WCA) of 150°, a maximum contact-angle hysteresis (CAH) of 10°, and a sliding angle (SA) less than 10° may efficiently enable water and water-soluble contaminants to easily roll off the coating surface, leaving little or no residue, and carrying away any surface pollutants originally present [9-12]. Therefore, an industrially producible and practically applicable super-water-repellent self-cleaning gray solar reflective concrete pavement coating was developed in our laboratory from commercially available materials.

In the current work, the super-water-repellent self-cleaning properties and the surface morphology of the solar reflective concrete pavement coating are analyzed and discussed. Moreover, the optical properties of the solar reflective concrete pavement coating and those of conventional concrete pavements, including their glossiness, lightness, and spectral reflectance, are investigated and compared. The thermal performance is evaluated and the cooling effect of the developed solar reflective pavements is estimated. Finally, the self-cleaning and optical properties of the coating after artificial accelerated weathering are studied and discussed.

MATERIAL AND METHODS

Selection of materials

To manufacture the coating, a styrene-acrylic emulsion, grade EC0702, was purchased from BASF Corporation to be used as a water-based binder. Meanwhile, to modulate the color of the coating in order to ensure a match with concrete pavement, the following spectral-selective pigments were employed: titanium dioxide rutile, grade Ti-Pure^{TM} R-902, purchased from DuPont Chemicals Co., Ltd.; titanium dioxide, grade Altiris® 550, generously supplied by Huntsman Corporation; and commercially available pigments including dioxazine purple, chrome titanium yellow, cobalt titanate green, and Cromophtal® Orange. Furthermore, an octyltriethoxysilane was purchased from Dow Corning Company to chemically modify the selected functional fillers.

Preparation of superhydrophobic surface

The pretreatment of functional fillers is necessary in this work. The prescribed quantities of heavy calcium carbonate and octyltriethoxysilane were added into a mixing setup and the mixture was stirred at high speed for 60 min. Subsequently, the mixture was filtered and the obtained powder was dried at 110 °C and ground to prepare the superhydrophobic solar reflective pavement coating. To construct superhydrophobic surfaces, a pneumatic angle grinder equipped with silicon carbide emery papers with various grit numbers (80, 120, 180, 240, 320, and 500) was employed in this work for roughening of the coating surfaces.

Characterization of self-cleaning properties

For a systematic evaluation of the self-cleaning properties of the super-water-repellent solar reflective concrete pavement coating developed in this work, the static WCA, the dynamic CAH, and SA were measured on an OCA 15EC (DataPhysics Instruments GmbH, Germany) contact-angle system at ambient temperature using 5 µL, 5 µL, and 10 µL water droplets, respectively. The reported values of CA, CAH, and SA were calculated as the average of five measurements, unless otherwise indicated. The morphologies of the resultant coating surfaces were determined using a Zeiss-supra 55 field emission Scanning Electron Microscopy.

Measurements of cooling properties

The spectral reflectance of the created gray solar reflective pavement coating was examined using a UV-VIS-NIR spectrophotometer (Perkin Elmer Lambda750) equipped with an integrating sphere (150 mm diameter, LabsphereRSA-PE-19) following ASTM E903-96. The lightness and the glossiness of the coating were determined using a color reader (CR-10, Konica Minolta Sensing, Inc.) and a vancometer (HP-380, Shanghai Hanpu Optoelectric Technology Co. Ltd.), respectively. Measurement of thermal emittance is following ASTM C 1371 (Standard test method for determining the emittance of materials near room temperature using portable emissometers), a portable differential thermopile emissometer AE1 (Devices & Services Co., Dallas, TX) was used to measure the thermal emittances of the coatings.

Artificial accelerated weathering tests

The artificial accelerated weather resistance of the solar reflective gray pavement coating was evaluated using a xenon lamp weather resistance test chamber (SN-66, Beijing Beifang Lihui Test Instrument Equipment Co., Ltd.) following ISO 11341-2004. After 240 h, the exposure was completed and the spectral reflectance and super-water-repellency were examined again.

RESULTS AND DISCUSSION

Super-water-repellency

In principle, a super-water-repellent surface can be created either by roughening an intrinsically hydrophobic surface or by chemically modifying an inherently rough surface [10, 12]. The solar reflective concrete pavement coating with optimized formulation was sprayed onto a fiber cement board, thus producing a coating surface with an average WCA of (112 ± 0.5)°, which indicates that the coating has sufficiently low surface free energy (SFE). In order to increase the water-repellency of a coating surface beyond the upper limit, it is necessary to roughen the coating surface. Therefore, a pneumatic angle grinder equipped with emery papers of different grit numbers was used in this work to roughen the solar reflective concrete pavement coating surfaces.

1) Static water-repellency

Fig. 1 depicts the analysis of the static water-repellency of the solar reflective pavement coating. Fig. 1a presents the variation in the average WCA values, measured for the coating surfaces ground using emery papers with different grit numbers. Fig. 1b shows the dependence of the average WCA values on the grinding depth. Fig. 1c illustrates clearly the static super-water-repellency of different liquid droplets on the solar reflective concrete pavement coating, prepared by grinding with the 180-grit emery paper. The transparent and blue, white, green, red droplets were pure water and dyed water, emulsion used in this work, hydrochloric acid (1molL^{-1}) + methyl violet indicator, sodium hydroxide (1molL^{-1}) + phenolphthalein indicator, respectively. As observed in Fig. 1, roughening the solar reflective concrete pavement coating can increase significantly its water-repellency, with appropriate surface roughness being key to generating super-water-repellent surfaces, and the effects of grinding depth on the average CA values appeared to be negligible. The super-water-repellency of the coating surface showed good acid and alkali tolerance.

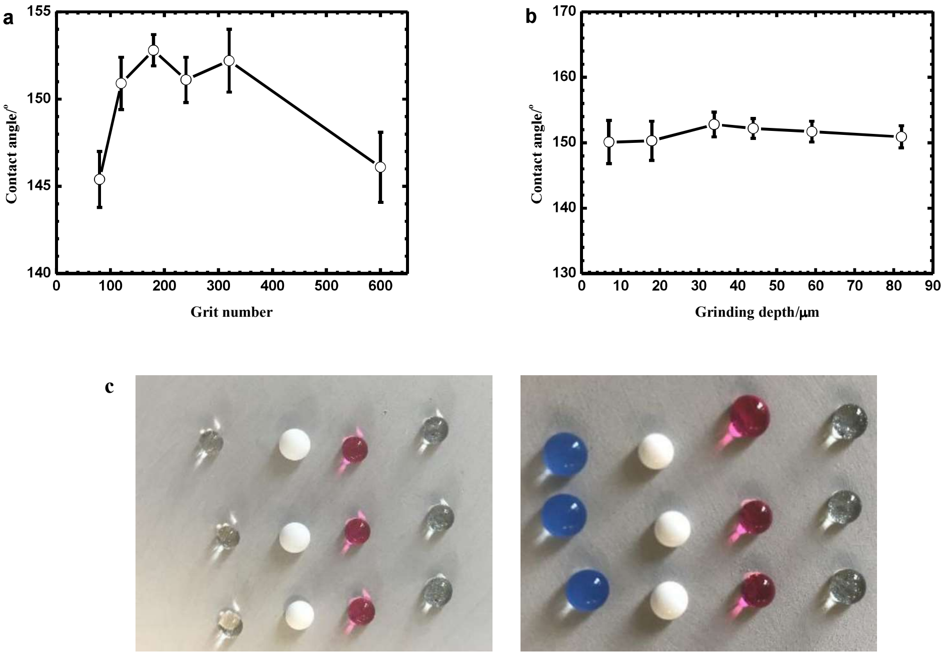

Fig.1. Static water-repellency of solar reflective concrete pavement coating.

2) Dynamic water-repellency and self-cleaning properties

Fig. 2 shows the dynamic water-repellency and self-cleaning properties of the solar reflective pavement coating prepared in this study. As shown in Fig. 2b, once the water droplet, released from the needle of the contact-angle testing device, hit the coating surface, it rolled off quickly from left to right following in an accelerated motion. As displayed in Fig. 2c, the dirty contaminants were effectively carried away from the coating surface by the water droplets, leaving no residue on the coating surface, exhibiting thus a pronounced "lotus effect".

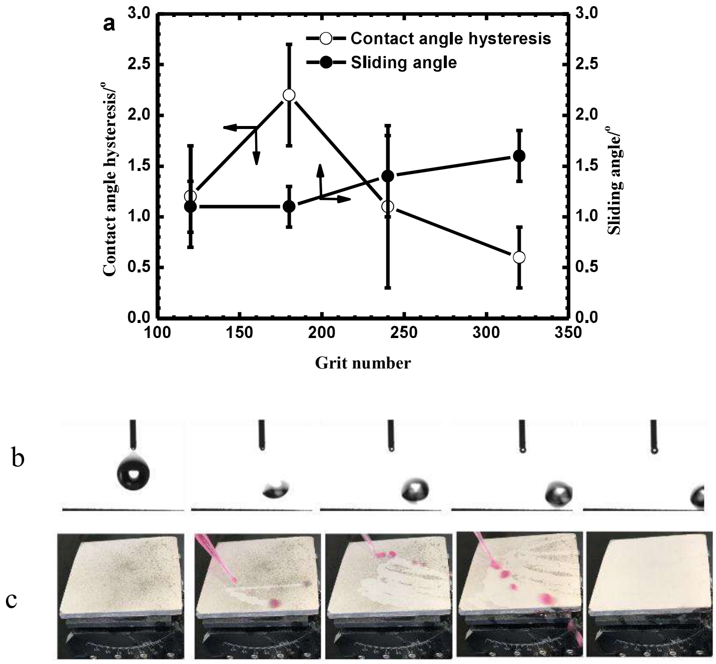

Fig.2. Dynamic water-repellency of solar reflective concrete pavement coating.

Surface morphology

The SEM images with low magnification obtained for the coating surfaces ground using emery papers with different grit numbers are presented in Fig. 3a–f, and the representative high-magnification SEM images measured for the coating surface ground using the 240-grit emery paper are shown in Fig. 3d (i)–(iii). As observed in Fig. 3a–f, the surface roughening resulted in the formation of many randomly distributed grooves on the coating surfaces. As observed in Fig. 3d (i)–(iii), many micro- and nano-particles (pigments and extenders) were exposed on the coating surfaces after the surface treatment, showing hierarchical surface structures.

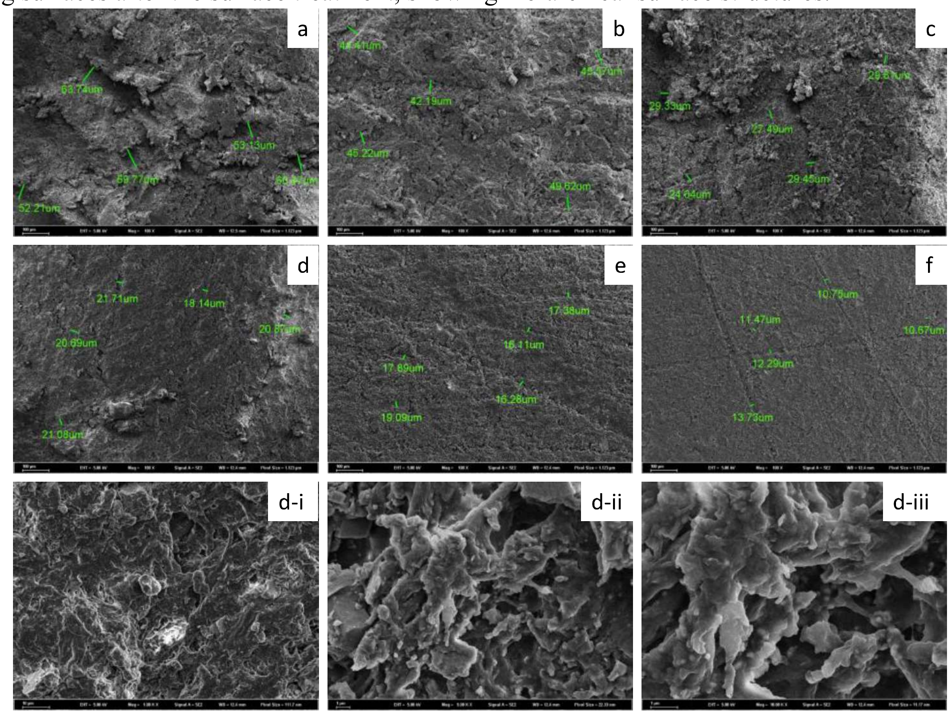

Fig.3. Low-magnification SEM images obtained for coating surfaces ground using emery papers with grit numbers of 80 (a), 120 (b), 180 (c), 240 (d), 320 (e), and 600 (f). Representative high-magnification SEM images obtained for the coating surface ground using emery paper with a grit number of 240.

Suitable surface roughness enables the fabricated grooves to trap air, which provides a floating or capillary force against the liquid droplets, and is a key factor for achieving small CAH and low SA values [12, 14-16]. As a consequence, the wettability of coating surfaces enters the "slippy" Cassie–Baxter regime [14] with low adhesion between liquid droplets and surfaces [12, 16]. Emery papers with grit numbers greater than 400 are generally used to polish surfaces to a mirror finish and therefore, the coating surface ground using the 600-grit emery paper is not sufficiently rough, resulting in smaller average WCA. The results of this study indicate that super-water-repellent self-cleaning surfaces can be fabricated simply by appropriate double scale surface roughness.

Optical properties of the coating

1) Establishment of concrete-gray color

An exactly non-metameric match to the concrete-gray color is desirable for the formulation and practical applications of a gray solar reflective pavement coating. Additionally, to solve the glare problems resulting from the increased solar reflectance of the gray solar reflective pavement coating, the glossiness of the coating should also be as similar to that of the concrete pavement as possible.

As pointed out in previous works [17-19], the desired color of a coating is commonly specified by the coating's VIS reflectance and optical lightness L* and its chromaticity coordinates a* and b*, defined by the device-independent CIE $L^*a^*b^*$ (Commission Internationale de l'Eclairage, CIE), which describes all of the colors visible to the human eye and has been created to serve as a model to be used as a reference. Table 1 compares the average lightness and glossiness values. As indicated in Table 1, the gray solar reflective pavement coating and the concrete pavements exposure displayed greenish and yellowish colors. Furthermore, both the lightness and glossiness of the concrete pavement were reduced after the outdoor exposure. Concurrently, while the a* value of the original concrete pavement changed from −2.0 to −0.8, its b* value changed from 6.7 to 9.1 as a result of this exposure. Overall, therefore, the lightness and glossiness values of the gray solar reflective pavement coating were closer to those of the original Portland cement concrete pavement than those of the concrete pavement after the outdoor exposure.

Table 1. The average lightness and glossiness values determined for the gray solar reflective pavement coating as well as for concrete pavements before and after outdoor exposure for approximately three years.

Samples	Lightness			Glossiness		
	L^*	a^*	b*	20°	60°	85°
Portland cement concrete pavement	69.2	−2.0	6.7	0.8	1.5	0.9
Concrete pavement after outdoor exposure	55.4	−0.8	9.1	0.7	0.9	0.3
Solar reflective pavement coating	73.0	−2.6	3.3	1.1	1.9	0.7

2) Optical and thermal properties

The overall solar reflectance values calculated for titanium dioxide rutile, Cromophtal® Orange, dioxazine purple, chrome titanium yellow, and cobalt titanate green were 0.910, 0.618, 0.334, 0.609, and 0.249, respectively.

Several phenomena can be observed in Fig. 4. Firstly, the spectral reflectance curve of the gray solar reflective coating in the VIS region lies between the spectral reflectance curves of the high visibility reflective coatings pigmented singly with titanium dioxide rutile, Cromophtal® Orange, and chrome titanium yellow, and those of low visibility reflective coatings filled singly with cobalt titanate green and dioxazine purple, as a result of the combined action of these cool pigments. Secondly, the shape of the curve arising from the gray solar reflective pavement coating in the shorter NIR region between approximately 700 and 900 nm was similar to those of singly pigmented coatings prepared with chrome titanium yellow, cobalt titanate green, and dioxazine purple, with a very small dip corresponding to the reflectance dip arising from the Cromophtal® Orange coating. Thirdly, a slightly narrower reflectance dip was observed in the spectral reflectance curve of the gray solar reflective pavement coating in the NIR region between approximately 900 to 1800 nm, which corresponds to the wide and deep reflectance dip of cobalt titanate green coating detected typically in this NIR region.

Additionally, in the VIS region, the spectral reflectance of the gray solar reflective pavement was slightly higher than that of the original Portland cement pavement coating. This observation, together with the results listed in Table 1, clearly indicate that a metameric match to the desired concrete color was achieved successfully by tailoring the weight proportions of the five solar reflective pigments employed in this work.

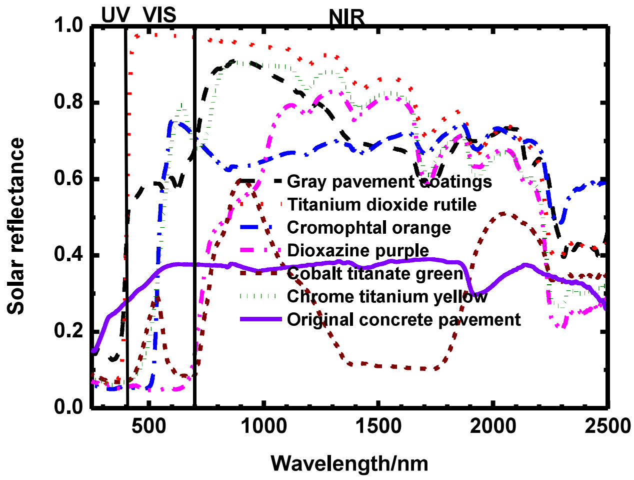

Fig.4. The spectral reflectance curves measured for the gray solar reflective pavement coating, the original Portland cement concrete pavement, and the coatings with different pigment.

As shown in Table 2, the overall solar reflectance values of the gray solar reflective pavement coating and the original concrete pavement were 0.683 and 0.356. The thermal emittance values measured for the gray solar reflective pavement coating and the original concrete pavement were 0.89 and 0.95, respectively. These four values were used to estimate the cooling effect of the gray solar reflective pavement coating relative to the concrete pavements before and after outdoor exposure for approximately 3 years.

Table 2. Spectral and solar reflectance values, together with thermal emittance values, measured for the designed coating and the original concrete pavement before outdoor exposure.

Samples	Solar reflectance	UV reflectance	VIS reflectance	NIR reflectance	Thermal emittance
Pavement coating	0.683	0.147	0.620	0.805	0.87
Concrete pavement	0.356	0.253	0.351	0.371	0.95

3) Estimated surface temperatures and cooling effect

The surface temperature of a coating may either be measured under sun exposure on a calm sunny summer day [18] or estimated from the measured solar reflectance and thermal emittance of the coating according to ASTM E 1980-11under standard conditions as follows: insolation = 1000 Wm^{-2}, sky temperature = 300 K, ambient air temperature = 310 K, and convection coefficient (medium wind) = 12 $Wm^{-2}K^{-1}$ [18,19]. Therefore, the surface temperatures of the original and outdoor exposed concrete pavements, as well as that of the gray solar reflective coating, and hence the cooling effect of the gray solar reflective coating relative to the concrete pavements will be estimated in this paper. The real cooling effect of the gray solar reflective coating will be tested in the field.

Fig. 5 depicts the time dependence of the solar reflectance for the outdoor exposed concrete pavement. The solar reflectance was measured to be approximately 0.174. As mentioned above, the solar reflectance of the original Portland cement concrete pavement was measured as 0.365. The thermal emittance measured for the concrete pavement after outdoor exposure was 0.94.

The surface temperatures for the gray solar reflective pavement coating, the original concrete pavement, and the concrete pavement after outdoor exposure were estimated to be 51.8, 66.9, and 75.8 °C. Accordingly, the cooling effect values of the gray solar reflective pavement coating calculated relative to the original concrete pavement and the concrete pavement after outdoor exposure for approximately three years are 15.1 and 24.0 °C, respectively. Such strong cooling effects can reduce significantly the surface temperature of concrete pavements in summer and effectively mitigate the UHIE caused by concrete pavements, providing that the gray solar reflective pavement coating are applied extensively to new concrete pavements and/or to existing concrete pavements for energy-efficient retrofit.

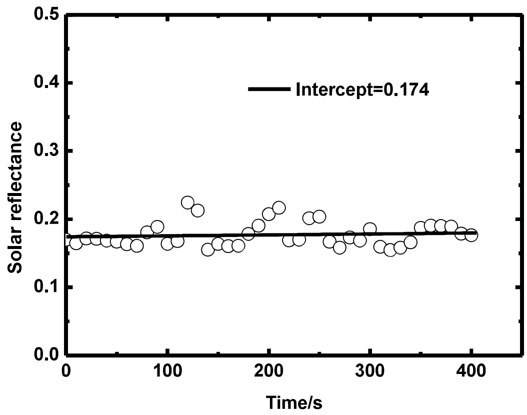

Fig. 5. The solar reflectance measured with two pyrometers on a clear and calm day for the concrete pavement after outdoor exposure for approximately three years.

The coating durability

It is widely accepted that mechanical contact [14, 20, 21], rain [22], and sunlight [22] can damage the super-water-repellency of natural super-water-repellent plants and artificial super-repellent coating surfaces exposed to an outdoor environment. It is important to investigate the long-term performance of the super-water-repellent self-cleaning solar reflective concrete pavement coating prepared in this study.

After 240 h of artificial accelerated weathering, the coating surface had an average WCA of (136.0 ± 6.4)°. Although the super-water-repellency of the coating surface was lost, the coating surface remained ultra-water-repellent. The loss of super-water-repellency of the weathered coating might be attributed to (i) the degradation of the low-surface-free-energy materials on the super-water-repellent coating surface as a result of UV exposure (xenon lamp irradiation), and (ii) micro-structure damage caused by periodic spraying with water by the tester.

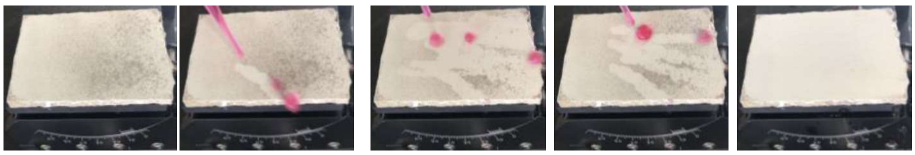

Fig.6. Snapshots of the self-cleaning process observed for the weathered coating surface tilted at a slope angle of 2° after being ground with the 180-grit emery paper.

As visually observed from Fig. 6, after 240 h of artificial accelerated weathering, the sample was free of cracking, chalking, blistering, peeling, and color change/fading. After the secondary surface roughening, static and dynamic wetting behaviors of the weathered coating surface were measured. As expected, the weathered coating surface after surface roughening had average WCA, CAH, and SA values of (151.7 ± 1.0), (4.4 ± 1.5), and (0.6 ± 0.4)°, respectively. Fig. 6 clearly illustrates the restored self-cleaning ability of the weathered coating surface at a slope angle of 2° after it was ground using the 180-grit emery paper. The behavior observed in Fig. 6 is nearly identical to that shown in Fig. 2c, with the exception of a smaller slope angle. Evidently, artificial accelerated weathering destroyed mainly the surface structures and degraded only the low-surface-free-energy materials on the outermost layer of the coating surface.

Fig. 7 compares the spectral reflectance curves of the solar reflective concrete pavement coating determined in its initial and artificially weathered states. As indicated in Fig. 7, after weathering, the spectral reflectance curve of the solar reflective pavement coating shifted downwards (i.e., to lower reflectance) over nearly the entire spectrum. Specifically, the percentage decreases in UV, VIS, NIR and the associated solar reflectance values were 15.6%, 8.2%, 6.7%, and 5.3%, respectively. Generally speaking, the attenuation of the solar reflectance stems mainly from the changes in physical and chemical compositions of the surface, and dirtying of the surface (particulate accumulation and biological growth) [23]. Since there was no soling on the coating surface during the artificial accelerated weathering, the attenuation of the spectral and solar reflectance values could be attributed to the changes in physical and chemical compositions of the surface.

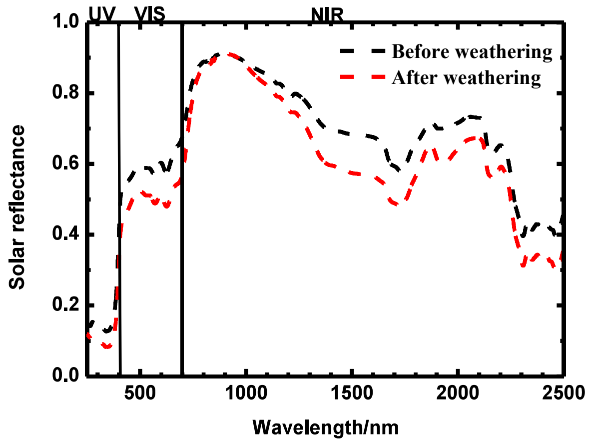

Fig. 7. The comparison of spectral reflectance curves of the solar reflective pavement coating before and after the 240-h artificial accelerated weathering test.

CONCLUSIONS

The experimental results presented above allow us to draw the following conclusions:

1. A largely producible, practically applicable, and easily restorable super-water-repellent self-cleaning solar reflective concrete pavement coating can be fabricated readily from commercially available low-cost materials via simple chemical and physical modification steps.

2. Grinding the low-surface-free-energy coating surfaces using emery papers with grit numbers of 120, 180, 240, and 320 yields micro-grooves and exposes micro- and nano-particles on the surfaces of coatings. Both the appropriately sized micro-grooves and micro- and nano-particles endow the coating surfaces with super-water-repellency and self-cleaning properties.

3. In terms of appearance, the color of the optimized solar reflective concrete pavement coating represents a metameric match to the desired concrete-color. The solar reflective concrete pavement coating is estimated to yield cooling effects of 15.1 and 24.0 °C, respectively, on a typical hot summer day.

4. Grinding the weathered coating surface with the 180-grit emery paper imparted the coating with appropriately sized micro-grooves, thereby enabling the weathered coating surface to completely regenerate its super-water-repellency and self-cleaning ability.

ACKNOWLEDGEMENT

The authors thank the financial support provided by the Technical Center of China State Construction Engineering Co., Ltd. (Grant No. 00.000.072).

REFERENCES

[1] M. SANTAMOURIS, A. SYNNEFA, *Using advanced cool materials in the urban built environment to mitigate heat islands and improve thermal comfort conditions*, Sol. Energy 85 (2011) 3085-3102.
[2] A. SYNNEFA, T. KARLESSI, N. GAITANI, M. SANTAMOURIS, D.N. ASSIMAKOPOULOS, C. PAPAKATSIKAS, *Experimental testing of cool colored thin layer asphalt and estimation of its potential to improve the urban microclimate*, Build. Environ. 46 (2011) 38-44.
[3] M. SANTAMOURIS, K. PAVLOU, A. SYNNEFA, K. NIACHOU, D. KOLOKOTSA, *Recent progress on passive cooling techniques. Advanced technological developments to improve survivability levels in low - income households.* Energy Build. 39 (2007) 859-66.

[4] H. E. GILBERT, P. J. ROSADO, G. BAN-WEISS, J. T. HARVEY, H. LI, B. H. MANDEL, D. MILLSTEIN, A. MOHEGH, A. SABOORI, R. M. LEVINSON, *Energy and environmental consequences of a cool pavement campaign.* Energy Build 157 (2017) 53-77.

[5] H. LI, J. HARVEY, Y. HE, Z. CHEN, P. LI, *Pavement treatment practices and dynamic albedo change in urban pavement network in California. Transportation Research Record:* Journal of the Transportation Research Board 2523 (2015) 145-155.

[6] A. MOHAJERANI, J. BAKARIC. *The urban heat island effect, its causes, and mitigation, with reference to the thermal properties of asphalt concrete,* J. Environ. Manage.197 (2017) 522-538.

[7] M. ZHENG, L. HAN, F. WANG, H. MI, Y. LI, L. HE, *Comparison and analysis on heat reflective coating for asphalt pavement based on cooling effect and anti-skid performance,* Constr. Build. Mater. 93 (2015) 1197–1205.

[8] Y. SHI, Z. SONG, W. ZHANG, J. SONG, J. QU, Z. WANG, Y. LI, L. XU, J. LIN, *Physicochemical properties of dirt-resistant cool white coatings for building energy efficiency*, Sol. Energy Mater. Sol. Cells 110 (2013) 133–139.

[9] G. E. KYRIAKODISA, M. SANTAMOURISA, *Using reflective pavements to mitigate urban heat island in warm climates - Results from a large scale urban mitigation project,* Urban Climate. https://doi.org/10.1016/j.uclim.2017.02.002

[10] A. ABDULHUSSEIN, G. KANNARPADY, A. WRIGHT, A. GHOSH, A. BIRIS, *Current trend in fabrication of complex morphologically tunable superhydrophobic nano scale surfaces,* Appl. Surf. Sci. 384 (2016) 311–332.

[11] J. O. F. WEST, G. W. CRITCHLOW, D. R. LAKE, R. BANKS, *Development of a superhydrophobic polyurethane-based coating from a two-step plasma-fluoroalkyl silane treatment,* Inter. J. Adhesion & Adhesives 68 (2016) 195–204.

[12] N. VALIPOUR M, F. CH. BIRJANDI, J. SARGOLZAEI, *Super-non-wettable surfaces: A review,* Colloids and Surfaces A: Physicochem. Eng. Aspects 448 (2014) 93–106.

[13] L. ZHOU, S. XU, G. ZHANG, D. CAI, Z. WU, *A facile approach to fabricate self-cleaning paint,* Appl. Clay Sci. 132–133 (2016) 290–295.

[14] J. GENZER, K. EFIMENKO, *Recent developments in superhydrophobic surfaces and their relevance to marine fouling: a review,* Biofouling 22 (2006) 339–360.

[15] C. AULIN, S.H. YUN, L. WÅGBERG, T. LINDSTROM, *Design of highly oleophobic cellulose surfaces from structured silicon templates,* ACS Appl. Mater. Interfaces 1 (2009) 2443–2452.

[16] C. T. HSIEH, F. L. WU, W. Y. CHEN, *Super water- and oil-repellencies from silica-based nanocoatings,* Surf. Coat. Technol. 203 (2009) 3377–3384.

[17] R. F. BRADY, L. V. WAKE, *Principles and formulations for organic coatings with tailored infrared properties,* Prog. Org. Coat. 20 (1992) 1–25.

[18] X. XUE, J. QIN, J. SONG, J. QU, Y. SHI, W. ZHANG, Z. SONG, L. JIANG, J. LI, H. GUO, T. ZHANG, *The methods for creating energy efficient cool gray building coatings—Part I: Preparation from white and black pigments,* Sol. Energy Mater. Sol. Cells. 130 (2014) 587–598.

[19] J. QIN, J. SONG, J. QU, X. XUE, W. ZHANG, Z. SONG, *The methods for creating building energy efficient cool black coatings,* Energy Build. 84 (2014) 308–315.

[20] D. Y. NADARGI, R. R. KALESH, A.V. RAO, *Rapid reduction in gelation time and impregnation of hydrophobic property in the tetra-ethoxysilane (TEOS) based silica aerogels using NH_4F catalyzed single step sol–gel process,* Journal of Alloys and Compounds 480 (2009) 689–695.

[21] W. C. WU, X. L. WANG, X. J. LIU, F. ZHOU, *Spray-coated fluorine-free superhydrophobic coatings with easy reparability and applicability*, ACS Appl. Mater. Interfaces. 1 (2009) 1656–1661.

[22] S. A. MAHADIK, P. D. FERNANDO, N. D. HEGADE, *Durability and restoring of superhydrophobic properties in silica-based coatings,* J. Colloid and Interface Sci. 405 (2013) 262–268.

[23] P. BERDAHL, H. AKBARI, R. LEVINSON, W. A. MILLER, *Weathering of roofing materials —an overview,* Constr. Build. Mater. 22 (2008) 423–433.