RESEARCH, DEVELOPMENT & TECHNOLOGY TRANSFER
QUARTERLY PROGRESS REPORT

Wisconsin Department of Transportation
DT1241 4/2010

INSTRUCTIONS:
Research project investigators and/or project managers should complete a quarterly progress report (QPR) for each calendar quarter during which the projects are active.

WisDOT research program category: ☐ Policy research ☒ Wisconsin Highway Research Program ☐ Other ☐ Pooled fund TPF#		Report period year: 2010 ☐ Quarter 1 (Jan 1 – Mar 31) ☐ Quarter 2 (Apr 1 – Jun 30) ☐ Quarter 3 (Jul 1 – Sep 30) ☒ Quarter 4 (Oct 1 – Dec 31)
Project title: Superhydrophobic Engineered Cementitious Composites for Highway Bridge Applications: Phase I		
Project investigator: Konstantin Sobolev	Phone: (414) 229-3198	E-mail: sobolev@uwm.edu
Administrative contact: Peggy Vanco	Phone: (414) 229-4853	E-mail: pvanco@uwm.edu
WisDOT contact: Jim Parry	Phone:	E-mail:
WisDOT project ID: n/a	Other project ID: CFIRE 04-09	Project start date: 10/1/2010
Original end date: 9/30/11	Current end date: 9/30/2011	Number of extensions: 0

Project schedule status:
☒ On schedule ☐ On revised schedule ☐ Ahead of schedule ☐ Behind schedule

Project budget status:

Total Project Budget	Expenditures Current Quarter	Total Expenditures	% Funds Expended	% Work Completed
$75,786.00	$10,005.00	$10,005.00	13%	25%

Project description:
The strength and durability of highway bridges are the key components in maintaining a high level of freight transportation capacity on the nation's highways [1-5]. Highways, bridges, and other critical transportation infrastructure works are rapidly deteriorating due to loading and deformation, aging, de-icing, and other detrimental factors in addition to rebar corrosion [1-5]. The average service life of concrete infrastructure in Wisconsin is 40-50 years, with up to 10% of bridge decks reinforced by uncoated rebar needing replacement after 30 years [3, 6]. The direct costs for roadway improvements are escalating because the price of key materials needed for highway and bridge construction has increased rapidly (~46% from 2004) [2, 7]. Indirect costs of highway bridge construction, in the form of environmental damage, are being realized in relation to the production and recycling of basic concrete materials. The time is right for a paradigm change to address the urgent need for highly durable and more sustainable materials to meet the challenges that future freight transportation will demand.
The focus of the research project is to develop a new hybrid engineered cementitious composite (ECC) [8], using polyvinyl alcohol fibers and hydrophobic compounds, to create a substitute concrete which can provide the strength and durability demanded in key regions of highway bridges. Normal cement based concrete is a brittle material and inevitably develops cracking, often due to shrinkage during curing and extended after loading. A new generation of superhydrophobic ECC fiber reinforced concrete material, with enhanced durability and large ductility, will result in up to 120 year service life for critical parts of highway bridges as well as other concrete infrastructure components.
The superhydrophobic hybridization approach [9-12] is a highly effective method for controlling the durability of concrete with large volumes of mineral additives or byproducts used as cement replacements. The developed superhydrophobic ECC will meet the top sustainability benchmarks and serve as the next technological level for sustainable concrete infrastructure with high performance and long service life.
The first task of the project is to identify the composition and technological approach to produce the ECC with improved ductility and strain-hardening response. The next task is to produce different types of superhydrophobic admixtures and investigate the performance of ECCs with different dosages of superhydrophobic admixture (0.01 - 0.1% of cement weight).

Progress this quarter (includes meetings, work plan status, contract status, significant progress, etc.):
The durability of concrete bridges is often limited by the performance of connection regions or joints between bridge components, especially in decks. A current CFIRE project is investigating the use of precast bridge approach slabs that could reduce the early distress noted in service [13]. The connection between an approach slab and bridge deck, or joints in the bridge deck, or the portion of bridge deck bending in a negative curvature above mid-span bridge piers, are critical bridge locations where durability problems are apparent and premature deterioration occurs. This results in regular maintenance demands or early replacement. A high-performance material that does not exhibit early age shrinkage cracking, withstands the deformation demands from truck loading, and provides durability is required for these susceptible regions.
Engineered cementitious composite (ECC) materials exhibit very ductile performance under tension, like steel, for example, as shown in Fig. 1. The strain capacity of ECC may be increased by a factor of 200 when high-strength reinforcing fibers are three-dimensionally dispersed in the mortar [8, 14, 15]. This research was conducted with polyvinyl alcohol (PVA) (Kuralon K-II). The engineered fiber composite controls initial shrinkage cracking while providing extreme deformation and strain enhancement, as illustrated in our research team's previous results in Fig. 1, left.

Figure 1: The Strain-Hardening Performance of ECC

The research team at UW-Madison designed and tested for flexure the ECCs with cross-sectional dimensions of 1x3 in at a span of 11 in. The effect of the matrix strength (defined by the water-to-cement ratio - w/c from 0.24 to 0.33) on load-deflection behavior was investigated. The dosage of PVA fibers was 2% by volume and beams were tested at the age of nine days.

The initial test results were relatively similar within the ECC group with lower water-to-cement ratios, however, they were highly scattered at higher water-to-cement ratios. This may be caused by the pullout of the fibers from a weaker matrix at larger w/c ratios. The cracking pattern was observed to have multiple closely spaced cracks (Fig. 1, right), which were relatively small and then led to failure. During some tests, the specimens had larger cracks spaced about 1 in apart, which then led to failure. It was observed that load at first crack (at the end of the elastic region) depends on the w/c ratio reaching up to 250 lbs at w/c of 0.24. The maximum bending load and maximum load at failure of approximately 500 lbs and 400 lbs, respectively, were also realized at the lowest w/c.

The deflection behavior of tested ECC beams is controlled by interfacial bond and fiber pullout; therefore, significant scattering of experimental data was observed at higher water-to-cement ratios. The obtained ECC demonstrated strain-hardening performance, as shown in Fig. 2.

Figure 2: Load vs. deflection of flexural tests for PVA fibers in ECC.

In addition to improved deformability and crack control provided by ECC, this research aims to create a new high-performance material with improved long-term durability by combining ECC with superhydrophobic hybridization. Superhydrophobic hybridization of concrete is a novel concept developed at UW-Milwaukee, engaging interdisciplinary work combining biomimetics (lotus effect), chemistry (siloxane polymers) and nanotechnology (nano-SiO_2 particles) to resolve fundamental problems of concrete such as insufficient durability and corrosion resistance for internal reinforcing [9-12]. The use of a superhydrophobic admixture helps to tailor the volume, size, and distribution of air voids in the concrete, and the bond with PVA fibers to realize controlled pullout behavior. Furthermore, controlled air void structures can be used to realize the "preferred" fracture modes. These synergetic effects are verified by the research program.
The design of hybrid superhydrophobic ECC is based on three principles:
1. Micromechanical design of ECC with 1 to 4 % (by volume) of polyvinyl alcohol fibers to realize ductile performance.
2. Application of small quantities (0.01 to 0.1% of cement weight) of siloxane-based hydrophobic admixtures (e.g., based on polymethyl- hydrosiloxane, PEHS/PMHS) modified by super-fine submicro- or nano-sized materials (such as nano-silica, nano-clay additives or SiO_2-rich reactive powders) and use of an effective superplasticizer to form a controlled air-void structure (Figs. 3,4).
3. Inclusion of selected by-product or mineral additives (also known as supplementary cementitious materials, SCMs) to decrease cement content and improve the sustainable nature of the material.
Superhydrophobic surfaces, or surfaces that have a water contact angle Θ larger than 150° (Fig. 3), have generated much interest due to their potential in industrial applications (mainly for self-cleaning), and have been tested for enhancing concrete durability. This nature-inspired approach improves the performance of hydrophobic materials that control wettability [10-12].
UW-Milwaukee team manufactured superhydrophobic admixtures by combination of the hydrogen containing siloxane admixture (e.g., PMHS) with small quantities of super-fine, submicro- or nano-sized particles such as nano-silica, nano-clay

additives, or SiO2-rich reactive powders (Fig. 4).
A modified PEHS/PMHS admixture (used at a dosage of 0.01…0.1% of cement weight) releases hydrogen and forms a small (10 - 100 μm), uniform air void evenly distributed within the cement paste (Fig. 4, left). The volume, size, and distribution of the air void within the hardened cement phase are precisely tailored by preparing the water-based emulsion of siloxane with a certain droplet size. For optimal performance, more than 70% of the PEHS must be dispersed to the size of less than 10 μm [9]. As a result, the hydrophobic particles cover the surface of the voids, providing the superhydrophobic hybridization effect.

Figure 3: The Concept of Superhydrophobic Hybridization of Concrete Pore Surface

Fig. 4: How the Superhydrophobic Hybridization of Concrete Works

Furthermore, the research work at UW-Milwaukee focused on the proportioning and dispersion of hydrophobic/superhydrophobic (PMHS-based) admixtures needed to achieve the optimal volume, size, and distribution of air voids within the hardened paste to provide the long-term durability for the concrete/ECC. Different types of PMHS additive were produced (at different emulsification speeds and concentrations of emulsifying agent and nano-particle dosage) and characterized.
The application of the developed PMHS admixture in ECC will help to control the bond of PVA fibers and realize controlled pullout behavior rather than fiber rupture. Furthermore, the controlled air void structure can be used to design the "preferred" fracture modes. These synergetic effects will be further investigated.

References

1. Poor Infrastructure Fails America, Civil Engineers Report http://www.cnn.com/2009/US/01/28/infrastructure.report.card/index.html
2. Deteriorating Urban Pavement Conditions Cost the Average Driver More Than $400 Annually http://www.reuters.com/article/pressRelease/idUS101228+12-Mar-2008+PRN20080312
3. Tabatabai, H., Ghorbanpoor, A., and Turnquist-Nass, A., Rehabilitation Techniques for Concrete Bridges, WHRP Report 05-01, Wisconsin Highway Research Program, 2005, 310 pp.
4. Klaiber, F.W., Dunker, K.F., Wipf, T.J., Sanders, W.W., Methods of Strengthening Existing Highway Bridges. Transportation Research Record 1180, NRC, National Academy Press, 1988.
5. Hooks, J.A., Holding it together: FHWA Bridge Plan Part I, Roads & Bridges Magazine, 41(6), 2003.
6. Tabatabai, H., Tabatabai, M., and Lee, C., Reliability of Bridge Decks in Wisconsin, ASCE Journal of Bridge Engineering, 2010, in press.
7. Trends in Highway Material Costs http://www.wsdot.wa.gov/biz/construction/constructioncosts.cfm
8. Li, V.C., "Engineered Cementitious Composites – Tailored Composites Through Micromechanical Modeling," in Fiber Reinforced Concrete: Present and the Future. Eds. N. Banthia et al, CSCE, Montreal, 64-97, 1998.
9. Sobolev K. and Batrakov V., The Effect of a PEHSO on the Durability of Concrete with Supplementary Cementitious Materials. ASCE Journal of Materials in Civil Engineering, 19(10), 2007, 809-819.
10. Sobolev K. and Ferrada-Gutiérrez M., How Nanotechnology Can Change the Concrete World: Part 2. American Ceramic Society Bulletin, 11, 2005, 16-19.
11. Becky Poole, Biomimetics: Borrowing from Biology http://www.thenakedscientists.com/HTML/articles/article/biomimeticsborrowingfrombiology/
12. Kerstin Koch, Bharat Bhushan and Wilhelm Barthlott. Diversity of structure, morphology and wetting of plant surfaces, Soft Matter, 2008, 4, 1943 – 1963.
13. Oliva, M., Schneider, J., "An Innovative Focus on Highway Bridge Approach Slabs," proposal funded by the FHWA CFIRE National Transportation Center, July 2009
14. Zhang, J., H. Stang and V.C. Li, "Experimental Study On Crack Bridging In FRC Under Uniaxial Fatigue Tension," ASCE J. of Materials in Civil Engineering, Vol. 12, No. 1, pp. 66-73, 2000.
15. Li, V. C., "Advances in ECC Research," ACI Special Publication on Concrete: Material Science to Applications, SP 206-23, pp. 373-400, 2002.

Anticipated work next quarter:

- Produce and test superhydrophobic admixtures
- Establish online production of superhydrophobic admixtures
- Characterize mortars with superhydrophobic admixtures
- Test the mechanical behavior of superhydrophobic ECC

Circumstances affecting project or budget:
none

Attach / insert Gantt chart and other project documentation

FOR WISDOT USE ONLY

Staff receiving QPR:	Date received:
Staff approving QPR:	Date approved:

Description

The strength and durability of highway bridges are the key components in maintaining a high level of freight transportation capacity on the nation's highways [1-5]. Highways, bridges, and other critical transportation infrastructure works are rapidly deteriorating due to loading and deformation, aging, de-icing, and other detrimental factors in addition to rebar corrosion [1-5]. The average service life of concrete infrastructure in Wisconsin is 40-50 years, with up to 10% of bridge decks reinforced by uncoated rebar needing replacement after 30 years [3, 6]. The direct costs for roadway improvements are escalating because the price of key materials needed for highway and bridge construction has increased rapidly (~46% from 2004) [2, 7]. Indirect costs of highway bridge construction, in the form of environmental damage, are being realized in relation to the production and recycling of basic concrete materials. The time is right for a paradigm change to address the urgent need for highly durable and more sustainable materials to meet the challenges that future freight transportation will demand.

The focus of the research project is to develop a new hybrid engineered cementitious composite (ECC) [8], using polyvinyl alcohol fibers and hydrophobic compounds, to create a substitute concrete which can provide the strength and durability demanded in key regions of highway bridges. Normal cement based concrete is a brittle material and inevitably develops cracking, often due to shrinkage during curing and extended after loading. A new generation of superhydrophobic ECC fiber reinforced concrete material, with enhanced durability and large ductility, will result in up to 120 year service life for critical parts of highway bridges as well as other concrete infrastructure components.

The superhydrophobic hybridization approach [9-12] is a highly effective method for controlling the durability of concrete with large volumes of mineral additives or byproducts used as cement replacements. The developed superhydrophobic ECC will meet the top sustainability benchmarks and serve as the next technological level for sustainable concrete infrastructure with high performance and long service life.

The first task of the project is to identify the composition and technological approach to produce the ECC with improved ductility and strain-hardening response. The next task is to produce different types of superhydrophobic admixtures and investigate the performance of ECCs with different dosages of superhydrophobic admixture (0.01 - 0.1% of cement weight).

Progress

The durability of concrete bridges is often limited by the performance of connection regions or joints between bridge components, especially in decks. A current CFIRE project is investigating the use of precast bridge approach slabs that could reduce the early distress noted in service [13]. The connection between an approach slab and bridge deck, or joints in the bridge deck, or the portion of bridge deck bending in a negative curvature above mid-span bridge piers, are critical bridge locations where durability problems are apparent and premature deterioration occurs. This results in regular maintenance demands or early replacement. A high-performance material that does not exhibit early age shrinkage cracking, withstands the deformation demands from truck loading, and provides durability is required for these susceptible regions.

Engineered cementitious composite (ECC) materials exhibit very ductile performance under tension, like steel, for example, as shown in Fig. 1. The strain capacity of ECC may be increased by a factor of 200 when high-strength reinforcing fibers are three-dimensionally dispersed in the mortar [8, 14, 15]. This research was conducted with polyvinyl alcohol (PVA) (Kuralon K-II). The engineered fiber composite controls initial shrinkage cracking while providing extreme deformation and strain enhancement, as illustrated in our research team's previous results in Fig. 1, left.

Figure 1: The Strain-Hardening Performance of ECC

The research team at UW-Madison designed and tested for flexure the ECCs with cross-sectional dimensions of 1x3 in at a span of 11 in. The effect of the matrix strength (defined by the water-to-cement ratio - w/c from 0.24 to 0.33) on load-deflection behavior was investigated. The dosage of PVA fibers was 2% by volume and beams were tested at the age of nine days.

The initial test results were relatively similar within the ECC group with lower water-to-cement ratios, however, they were highly scattered at higher water-to-cement ratios. This may be caused by the pullout of the fibers from a weaker matrix at larger w/c ratios. The cracking pattern was observed to have multiple closely spaced cracks (Fig. 1, right), which were relatively small and then led to failure. During some tests, the specimens had larger cracks spaced about 1 in apart, which then led to failure. It was observed that load at first crack (at the end of the elastic region) depends on the w/c ratio reaching up to 250 lbs at w/c of 0.24. The maximum bending load and maximum load at failure of approximately 500 lbs and 400 lbs, respectively, were also realized at the lowest w/c.

The deflection behavior of tested ECC beams is controlled by interfacial bond and fiber pullout; therefore, significant scattering of experimental data was observed at higher water-to-cement ratios. The obtained ECC demonstrated strain-hardening performance, as shown in Fig. 2.

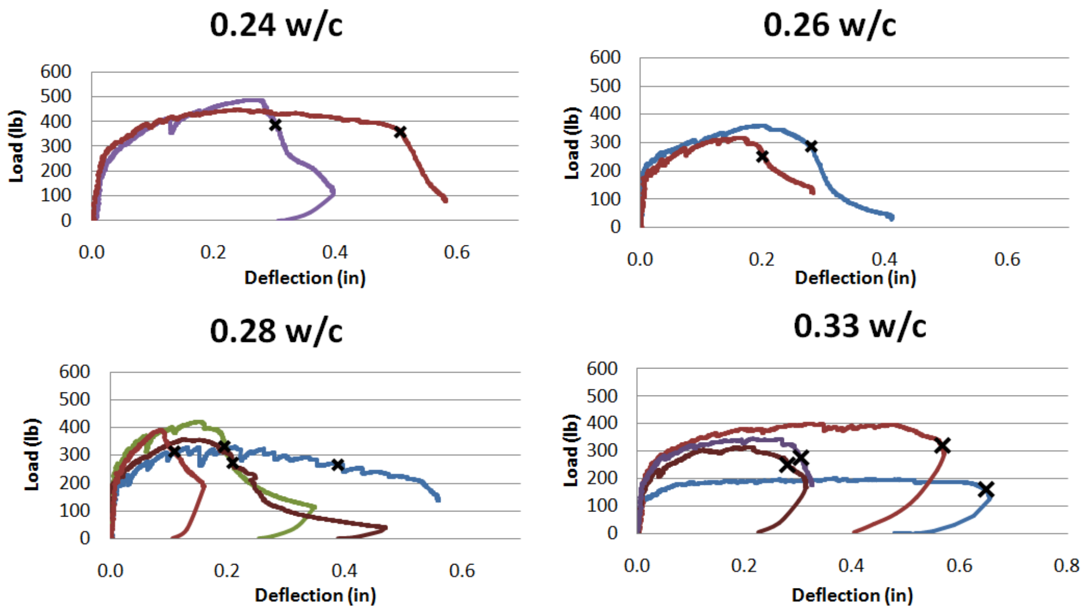

Figure 2: Load vs. deflection of flexural tests for PVA fibers in ECC.

In addition to improved deformability and crack control provided by ECC, this research aims to create a new high-performance material with improved long-term durability by combining ECC with superhydrophobic hybridization.

Superhydrophobic hybridization of concrete is a novel concept developed at UW-Milwaukee, engaging interdisciplinary work combining biomimetics (lotus effect), chemistry (siloxane polymers) and nanotechnology (nano-SiO_2 particles) to resolve fundamental problems of concrete such as insufficient durability and corrosion resistance for internal reinforcing [9-12]. The use of a superhydrophobic admixture helps to tailor the volume, size, and distribution of air voids in the concrete, and the bond with PVA fibers to realize controlled pullout behavior. Furthermore, controlled air void structures can be used to realize the "preferred" fracture modes. These synergetic effects are verified by the research program.

The design of hybrid superhydrophobic ECC is based on three principles:

1. Micromechanical design of ECC with 1 to 4 % (by volume) of polyvinyl alcohol fibers to realize ductile performance.
2. Application of small quantities (0.01 to 0.1% of cement weight) of siloxane-based hydrophobic admixtures (e.g., based on polymethyl- hydrosiloxane, PEHS/PMHS) modified by super-fine submicro- or nano-sized materials (such as nano-silica, nano-clay additives or SiO_2-rich reactive powders) and use of an effective superplasticizer to form a controlled air-void structure (Figs. 3,4).
3. Inclusion of selected by-product or mineral additives (also known as supplementary cementitious materials, SCMs) to decrease cement content and improve the sustainable nature of the material.

Superhydrophobic surfaces, or surfaces that have a water contact angle Θ larger than 150° (Fig. 3), have generated much interest due to their potential in industrial applications (mainly for self-cleaning), and have been tested for enhancing concrete durability. This nature-inspired approach improves the performance of hydrophobic materials that control wettability [10-12].

UW-Milwaukee team manufactured superhydrophobic admixtures by combination of the hydrogen containing siloxane admixture (e.g., PMHS) with small quantities of super-fine, submicro- or nano-sized particles such as nano-silica, nano-clay additives, or SiO_2-rich reactive powders (Fig. 4).

A modified PEHS/PMHS admixture (used at a dosage of 0.01…0.1% of cement weight) releases hydrogen and forms a small (10 - 100 μm), uniform air void evenly distributed within the cement paste

(Fig. 4, left). The volume, size, and distribution of the air void within the hardened cement phase are precisely tailored by preparing the water-based emulsion of siloxane with a certain droplet size. For optimal performance, more than 70% of the PEHS must be dispersed to the size of less than 10 μm [9]. As a result, the hydrophobic particles cover the surface of the voids, providing the superhydrophobic hybridization effect.

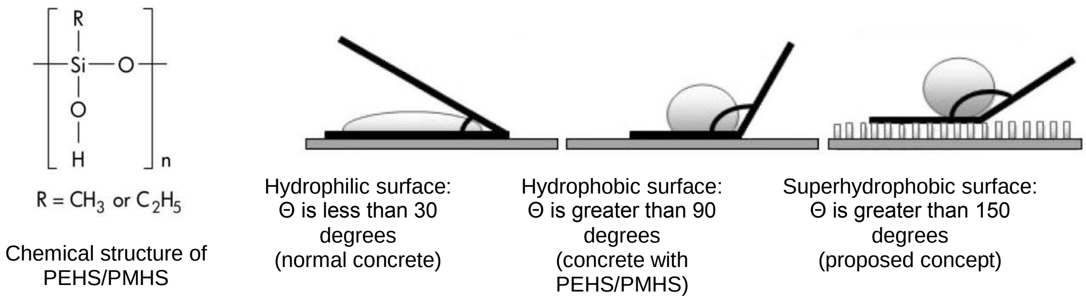

Figure 3: The Concept of Superhydrophobic Hybridization of Concrete Pore Surface

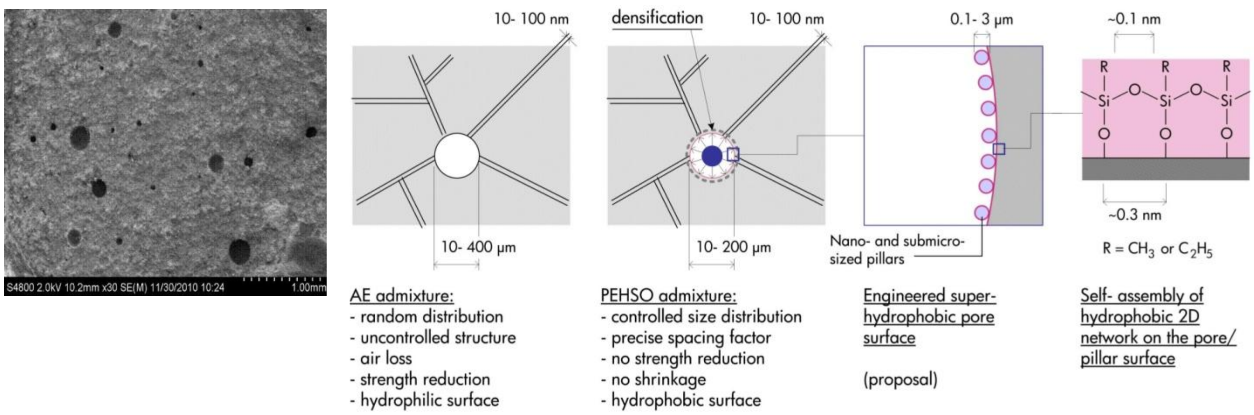

Fig. 4: How the Superhydrophobic Hybridization of Concrete Works

Furthermore, the research work at UW-Milwaukee focused on the proportioning and dispersion of hydrophobic/superhydrophobic (PMHS-based) admixtures needed to achieve the optimal volume, size, and distribution of air voids within the hardened paste to provide the long-term durability for the concrete/ECC. Different types of PMHS additive were produced (at different emulsification speeds and concentrations of emulsifying agent and nano-particle dosage) and characterized.

The application of the developed PMHS admixture in ECC will help to control the bond of PVA fibers and realize controlled pullout behavior rather than fiber rupture. Furthermore, the controlled air void structure can be used to design the "preferred" fracture modes. These synergetic effects will be further investigated.

References

1. Poor Infrastructure Fails America, Civil Engineers Report http://www.cnn.com/2009/US/01/28/infrastructure.report.card/index.html
2. Deteriorating Urban Pavement Conditions Cost the Average Driver More Than $400 Annually http://www.reuters.com/article/pressRelease/idUS101228+12-Mar-2008+PRN20080312

3. Tabatabai, H., Ghorbanpoor, A., and Turnquist-Nass, A., Rehabilitation Techniques for Concrete Bridges, WHRP Report 05-01, Wisconsin Highway Research Program, 2005, 310 pp.
4. Klaiber, F.W., Dunker, K.F., Wipf, T.J., Sanders, W.W., Methods of Strengthening Existing Highway Bridges. Transportation Research Record 1180, NRC, National Academy Press, 1988.
5. Hooks, J.A., Holding it together: FHWA Bridge Plan Part I, Roads & Bridges Magazine, 41(6), 2003.
6. Tabatabai, H., Tabatabai, M., and Lee, C., Reliability of Bridge Decks in Wisconsin, ASCE Journal of Bridge Engineering, 2010, in press.
7. Trends in Highway Material Costs http://www.wsdot.wa.gov/biz/construction/constructioncosts.cfm
8. Li, V.C., "Engineered Cementitious Composites – Tailored Composites Through Micromechanical Modeling," in *Fiber Reinforced Concrete: Present and the Futur*e. Eds. N. Banthia et al, CSCE, Montreal, 64-97, 1998.
9. Sobolev K. and Batrakov V., The Effect of a PEHSO on the Durability of Concrete with Supplementary Cementitious Materials. ASCE Journal of Materials in Civil Engineering, 19(10), 2007, 809-819.
10. Sobolev K. and Ferrada-Gutiérrez M., How Nanotechnology Can Change the Concrete World: Part 2. American Ceramic Society Bulletin, 11, 2005, 16-19.
11. Becky Poole, Biomimetics: Borrowing from Biology http://www.thenakedscientists.com/HTML/articles/article/biomimeticsborrowingfrombiology/
12. Kerstin Koch, Bharat Bhushan and Wilhelm Barthlott. Diversity of structure, morphology and wetting of plant surfaces, Soft Matter, 2008, 4, 1943 – 1963.
13. Oliva, M., Schneider, J., "An Innovative Focus on Highway Bridge Approach Slabs," proposal funded by the FHWA CFIRE National Transportation Center, July 2009
14. Zhang, J., H. Stang and V.C. Li, "Experimental Study On Crack Bridging In FRC Under Uniaxial Fatigue Tension," ASCE J. of Materials in Civil Engineering, Vol. 12, No. 1, pp. 66-73, 2000.
15. Li, V. C., "Advances in ECC Research," ACI Special Publication on Concrete: Material Science to Applications, SP 206-23, pp. 373-400, 2002.

Activities by month		2010			2011									Progress
		10	11	12	1	2	3	4	5	6	7	8	9	
Task 1	Purchase and Install Lab Equipment													100
	Develop Test Procedure for ECC													75
	Produce and Test ECC													50
Task 2	Produce and Test superhydrophic admixtures													20
	Establish Online Production of SHA													0
	Test the mechanical behavior of superhydrophobic ECC													0
	Characterize Mortars with SHA													0
	Optimize the characteristics of superhydrophobic ECC													0
	Perform the express evaluation of ECC durability													0