



MISSOURI
S&T

CENTER FOR TRANSPORTATION INFRASTRUCTURE AND SAFETY



Nano-Engineered Polyurethane Resin-Modified Concrete

by

G.S. Dhaliwal

Ph. D Candidate

Department of Mechanical and Aerospace Engineering

Faculty Advisors:

K. Chandrashekhara, J. Volz and T. Schuman



**NUTC
R345**

**A National University Transportation Center
at Missouri University of Science and Technology**



Disclaimer

The contents of this report reflect the views of the author(s), who are responsible for the facts and the accuracy of information presented herein. This document is disseminated under the sponsorship of the Department of Transportation, University Transportation Centers Program and the Center for Transportation Infrastructure and Safety NUTC program at the Missouri University of Science and Technology, in the interest of information exchange. The U.S. Government and Center for Transportation Infrastructure and Safety assumes no liability for the contents or use thereof.

Technical Report Documentation Page

1. Report No. NUTC R345	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle Nano-Engineered Polyurethane Resin-Modified Concrete	5. Report Date April 2014	6. Performing Organization Code
	7. Author/s G.S. Dhaliwal, K. Chandrashekhara, J. Volz and T. Schuman	
9. Performing Organization Name and Address Center for Transportation Infrastructure and Safety/NUTC program Missouri University of Science and Technology 220 Engineering Research Lab Rolla, MO 65409	8. Performing Organization Report No. Project # 00042529	10. Work Unit No. (TRAIS)
	11. Contract or Grant No. DTRT06-G-0014	
12. Sponsoring Organization Name and Address U.S. Department of Transportation Research and Innovative Technology Administration 1200 New Jersey Avenue, SE Washington, DC 20590	13. Type of Report and Period Covered Final	
	14. Sponsoring Agency Code	
15. Supplementary Notes		
16. Abstract The goal of the proposed work is to investigate the application of nano-engineered polyurethane (NEPU) emulsions for latex modified concrete (LMC). NEPU emulsions are non-toxic, environment friendly, durable over a wide temperature range, provide better adhesion, high strength, less cracking, and compatible with all mortar types. One of the weak links in a cement-aggregate composite material is the bond between the matrix and the aggregates. To improve the performance of the alternative cement binder (ACB), the research team intends to develop a NEPU resin to act as an intermediary between the aggregates and the ACB matrix. The NEPU will be used to precoat the aggregates prior to their placement within the ACB matrix. When combined with the ACB and water, the unhydrated ACB particles embedded within the NEPU-coated aggregates will react with the surrounding matrix during hydration, providing an enhanced interfacial zone and corresponding improvement in the material properties of the hardened material. In the proposed work, the used of bio-based NEPU emulsion for LMC application will also be investigated.		
17. Key Words Latex modified concrete, alternative cement binder, polymer portland cement concrete	18. Distribution Statement No restrictions. This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.	
19. Security Classification (of this report) unclassified	20. Security Classification (of this page) unclassified	21. No. Of Pages 17
22. Price		

**MISSOURI S&T – NATIONAL UNIVERSITY TRANSPORTATION CENTER
ADVANCED MATERIALS AND NON-DESTRUCTIVE TESTING TECHNOLOGIES**

Sequential #: R345

Project Title: Nano-Engineered Polyurethane Resin-Modified Concrete

GRA Support: Center for Infrastructure Engineering Studies

Graduate Student: G.S. Dhaliwal, Ph. D Candidate, Department of Mechanical and Aerospace Engineering

Faculty Advisors: K. Chandrashekhara, J. Volz and T. Schuman

Duration: 05/15/2013 – 12/31/2013

Project Summary: The goal of the proposed work is to investigate the application of nano-engineered polyurethane (NEPU) emulsions for latex modified concrete (LMC). NEPU emulsions are non-toxic, environment friendly, durable over a wide temperature range, provide better adhesion, high strength, less cracking, and compatible with all mortar types. One of the weak links in a cement-aggregate composite material is the bond between the matrix and the aggregates. To improve the performance of the alternative cement binder (ACB), the research team intends to develop a NEPU resin to act as an intermediary between the aggregates and the ACB matrix. The NEPU will be used to precoat the aggregates prior to their placement within the ACB matrix. When combined with the ACB and water, the unhydrated ACB particles embedded within the NEPU-coated aggregates will react with the surrounding matrix during hydration, providing an enhanced interfacial zone and corresponding improvement in the material properties of the hardened material. In the proposed work, the used of bio-based NEPU emulsion for LMC application will also be investigated.

Summary of Results: To improve the strength of concrete, the research team investigated the effects of introducing polyurethane (PU) and poly (vinyl alcohol co-ethylene) to act as an intermediary between the aggregates and the cement matrix. The polymers used were precoated to the aggregate prior to the placement of the aggregate in the cement matrix. The proposed modified concrete was subjected to mechanical testing. In this work, effects of different methods of making polymer modified concrete and effects of different amounts of polymer were investigated. It was observed that poly (vinyl alcohol co-ethylene) leads to an increase in flexure strength of concrete.

Introduction

Mortar and concrete made with portland cement have been popular construction materials in the world for the past 170 years or more. However, cement mortar and concrete have some disadvantages such as delayed hardening, low tensile strength, high drying shrinkage, and low chemical resistance. To reduce these disadvantages, polymer-modified concrete is used, which is made by the modifying ordinary cement mortar or concrete with polymer additives such as latexes, redispersible polymer powders, water-soluble polymers, liquid resins, and monomers. Polymer-modified mortars and polymer-modified concretes (PMC) have a monolithic co-matrix in which the organic polymer matrix and the cement gel matrix are homogenized [1]. The properties of polymer-modified mortar and concrete are determined by a co-matrix. In the systems modified with the latexes, redispersible polymer powders, and water-soluble polymers, the drainage of water from the systems along with the cement hydration leads to film or membrane formation. In the systems modified with the liquid resins and monomers, the addition of water induces the hydration of the cement and the polymerization of the liquid resins or monomers [2].

When polymer emulsions are mixed with portland cement concrete, the polymer forms a film coating on aggregate particles and cement grains, and seals any voids or microcracks. The resulting mixture of polymer emulsion and portland cement concrete has higher strength, high resistance to chloride penetration and is more inert to chemical attack than plain cement. PMC has been in commercial use since the 1950s. The raw materials and technology used in PMC production is similar to portland cement concrete except a colloidal suspension of polymer material in water (latex) is used as an admixture [3]. Due to its excellent bonding ability, high workability and high resistance to aggressive environments, PMC finds applications in overlays of industrial floors and rehabilitation of deteriorated bridge decks. The polymers that were conventionally used as latexes are polyvinyl acetate or polyvinylidene chloride. However, polyvinyl acetate has low wet strength and polyvinylidene chloride can cause corrosion of steel. These polymers were replaced by elastomeric polymers based on styrenebutadine and polyacrylate copolymers and have become more common latex materials [4,5]. Though styrenebutadine elastomeric polymer emulsions are commonly used today, they have a disadvantage of developing a brown colored coat when exposed to sunlight. As a result, these materials are unsuitable for patching applications where color match is important.

Scrivener et al. [6] has described in great detail the interfacial transition zone (ITZ) between cement paste and aggregate as the most important interface in concrete. Concrete is often considered to be two phase composite material i.e. cement paste plus aggregates. The origin of the ITZ lies in the so called "wall" effect of packing of cement grains against the relatively flat aggregate surface. This is directly responsible for the features of the ITZ, particularly its higher

porosity. Due to the way it is formed the ITZ is not a definite zone, but a region of transition. Its effective thickness varies with the micro structural feature being studied and during the course of hydration. As cement is a particulate material, the details of this transition zone are different around each aggregate particle. Individually cement paste and aggregates both show brittle elastic behavior, that is to say, linear, reversible deformation up to a limit, followed by sudden failure. In contrast, concrete, which is the composite material, shows significant quasi-ductile behavior [7]. The load bearing capacity continues to increase beyond the linear elastic limit and there is a progressive decrease in load bearing capacity after the peak load. Such behavior, which has important practical consequences, is due to the development of multiple microcracking predominantly in the ITZ. This well-known behavior leads to the common view of the ITZ as the weak link in concrete [8]. In this study, effect of PU and poly (vinyl alcohol co-ethylene) have been investigated to improve the ITZ, so as to improve the compressive strength and flexure strength of the concrete.

Sample Preparation

1. Compressive test samples

The experimentation was started by making the samples of pure concrete for compressive test, i.e. making concrete samples without any modification by polymer. The samples were prepared using the ratio of material as shown in the table 1. The samples made were cured in water for 28 days. This ratio of the material and curing time was kept constant for the further experimentation, where the aggregate was treated with the polymers as explained ahead.

Table 1. Composition of concrete (Parts by mass)

Ingredient	Quantity
Aggregate	4 parts
Sand	2 parts
Cement	1 part
Water	½ part

Different polymers were considered and various methods were employed for the manufacture of the PMC. The initial study was performed using Polyurethane (PU) purchased from Bayer Material Science. Three different methods were adopted for the making of polyurethane based PMC:

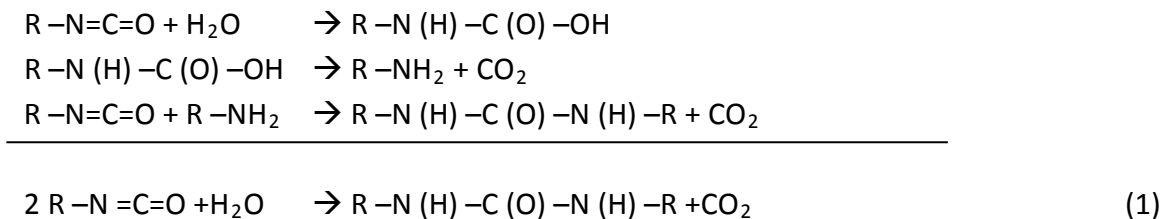
- Pre- cured aggregate
- Post cured aggregate
- Neat resin and aggregate

In the first method, pre-cured aggregate, the aggregate was treated with the PU resin and was cured. The aggregate particles after treating with PU resin were scattered on a plane surface as shown in figure 1, taking care that particles were not in contact with each other. If the aggregate particles stick together, it makes the aggregate unusable in the manufacturing of PMC. After the PU resin was cured, the aggregate was used in making PMC, in a conventional concrete manufacturing process. Using this method, three different categories of samples were prepared containing 30, 50 and 100 % of aggregate treated with PU. One disadvantage of this method is that it is cumbersome and time consuming. Therefore, the post cure method was identified which reduced manufacturing time and was less cumbersome.



Figure. 1. Aggregate particles treated with PU

In the post cured method, the aggregate was treated with PU resin and after 30 minutes, which is the gelation time of PU, aggregate was utilized in making PMC. The PMC poured in the molds was then cured in an oven. However the concrete did not harden. This can be explained by the chemical reaction between isocyanate, an active ingredient of PU with water as shown below (Equation 1).

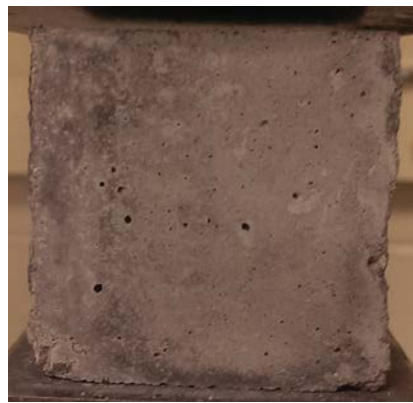


The reaction of isocyanate and water produces carbon dioxide. This results in the formation of foam. Because of this reaction, the cement-aggregate bonding did not take place. Therefore, this method was discontinued. The neat resin-aggregate method was then developed using neat PU resin.

In neat resin and aggregate method, the composition of concrete was aggregate and PU resin. No water was added to concrete in this method. The main advantage of this method was the quick cure time i.e. 8 hours at room temperature followed by 4 hours of heating in oven at 80° C (total 12 hours) as compared to cement concrete (7 to 28 days depending on the strength required). In neat resin concrete method, dry mixture of aggregate and cement was mixed with PU resin. No water was added to the concrete. The PU resin was cured in an oven. As cement was also added, after curing of PU, the specimens were kept in a water tank for 7 days for hydration of cement. Figure 2(a) shows a neat resin sample and figure 2(b) shows a sample made by 30 % aggregate coated by PU.



Figure. 2. (a) Neat resin specimen



(b) Specimen with 30% PU coated aggregate.

It was observed that isocyanate, an active component in PU is highly sensitive to water, which happens to be a key ingredient in making of concrete. This makes PU unfit for the commercial use. The need was felt for the application of a polymer which is not sensitive to water. Thus, the polymers soluble in water were looked upon. Polymers like poly (vinyl alcohol co-ethylene), poly (styrene co-vinyl acetate), and poly (styrene co- methyl methacrylate) were considered [9]. Since styrene based polymers have poor solubility in water, and their effect on the compressive strength of concrete has been investigated by other researchers [10, 11], they were not considered by the team for further testing. Poly (vinyl alcohol co-ethylene) purchased from Sigma Aldrich, which is soluble in a solution of water and propanol in 1:1 ratio was used for the further experimentation.

After the selection of the polymer, another important issue was the amount of the polymer to be utilized for making the specimens. Blum et al. [12-16] discussed the difference in the properties of the polymer when used in bulk and when adsorbed on the surface. Since the aim of the present work is to improve the ITZ, which is a thin zone around the aggregate, for the better bonding of the cement with aggregate particles. Different quantities of poly (vinyl alcohol co-ethylene) mixed with equal amount of propanol and water was used to treat the

aggregate. The aggregate is treated by dipping the measured amount of aggregate in the solution of measured quantity of poly (vinyl alcohol co-ethylene) dissolved in equal parts of water and propanol. The jar containing the above mentioned materials is kept on the hot plate and the solution is stirred continuously. As the propanol evaporates, poly (vinyl alcohol co-ethylene) ceases to be soluble and it forms a fine layer on the aggregate particles. This coated aggregate is used for the making of concrete.

Here it is important to discuss that to achieve the surface adsorbed polymer layer, as recommended by Blum et al., very small quantity of polymer, i.e. 2-6 mg/m² was used. To calculate the surface area of the aggregate, Image-J software was used as shown in figure 3, which helped in making a close approximation of the surface area of the aggregate.

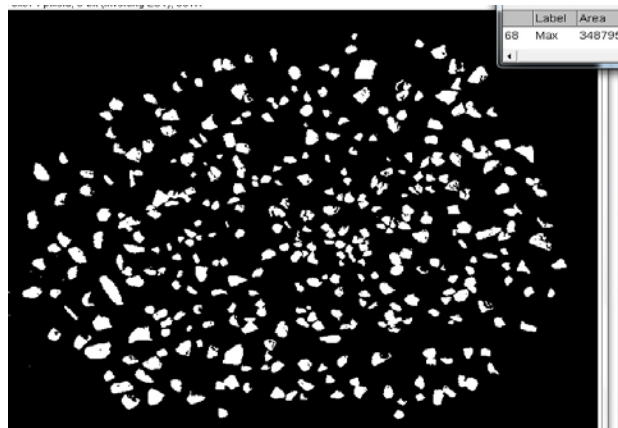


Figure. 3. Calculation of surface area of the aggregate

The various quantities of poly (vinyl alcohol co-ethylene) used for making samples are shown in Table 2.

Table 2. Quantity of polymer used in samples.

Sample	Quantity of polymer
I	2 mg/m ²
II	4 mg/m ²
III	6 mg/m ²
IV	10 g/m ²
V	20 g/m ²
VI	30 g/m ²

The samples I, II and III were made using the minimum amount of poly (vinyl alcohol co-ethylene), to ensure that polymer is adsorbed on the surface of the aggregate and does not forms a lump. Samples IV, V and VI are made by bulk amount of poly (vinyl alcohol co-ethylene). This is done to investigate the difference in the properties of PMC made by bulk and surface adsorbed polymer.

2. Flexure test samples

After making and testing the samples for compressive test (testing is explained in the next section), flexure samples were made. The materials were used as explained in table 1. With the experience gained from compression test sample preparation and testing, and the time constraint, the samples with following configuration were prepared:

- Pure concrete
- Pre-cured PU
 - 50% aggregate coated with PU
 - 100% aggregate coated with PU
- Poly (vinyl alcohol co-ethylene)
 - 6mg/m² of surface area of aggregate
 - 12mg/m² of surface area of aggregate



Fig.4 Pure concrete sample for flexure test.

Figure 4 shows the sample for flexure test with no polymer modification. The samples were prepared according to ASTM C31.

Testing of Samples

1. Compressive test

The prepared specimens were cured for 28 days each and were tested for compressive strength, according to ASTM C109 using the Tinius Olsen compression testing machine as shown in Figure 5.

Five samples of each category (Table 3) were prepared and the stress at failure was measured.



Fig.5 (a) 100% PU sample after compression test (b) Poly (vinyl alcohol co-ethylene) sample after compression test (c) Neat Resin sample after compression test

Table 3. Polymer quantity and stress at failure

Polymer	Quantity of polymer	No. of samples	Stress at failure (psi)
Pure Concrete	Nil	5	3636
Polyurethane (PU)	30%	5	3135
	50%	5	2889
	100%	5	2854
	Neat resin	5	11346
Poly (vinyl alcohol co-ethylene) surface adsorbed	2 mg/m ²	5	3518
	4 mg/m ²	5	3410
	6 mg/m ²	5	3272
Poly (vinyl alcohol co-ethylene) bulk	10 mg/m ²	5	3199
	20 mg/m ²	5	3147
	30 mg/m ²	5	3135

The comparison of the compressive strengths of all the samples (except neat resin) is shown in Figure 6.

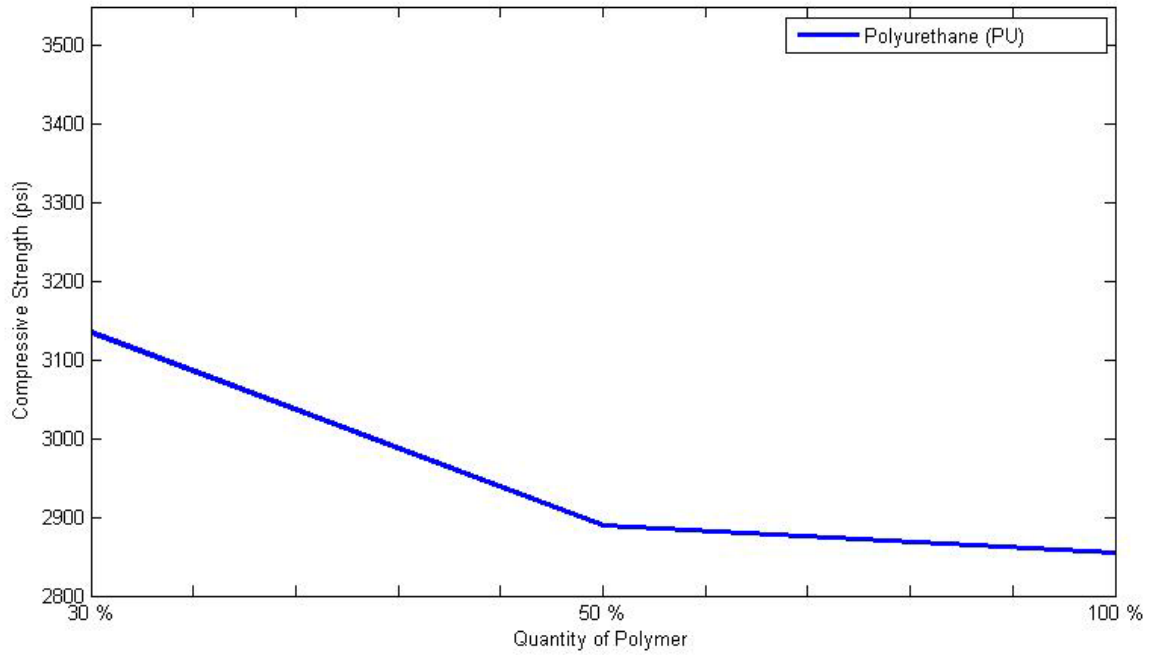


Figure 6 (a). Compressive strength vs quantity of PU

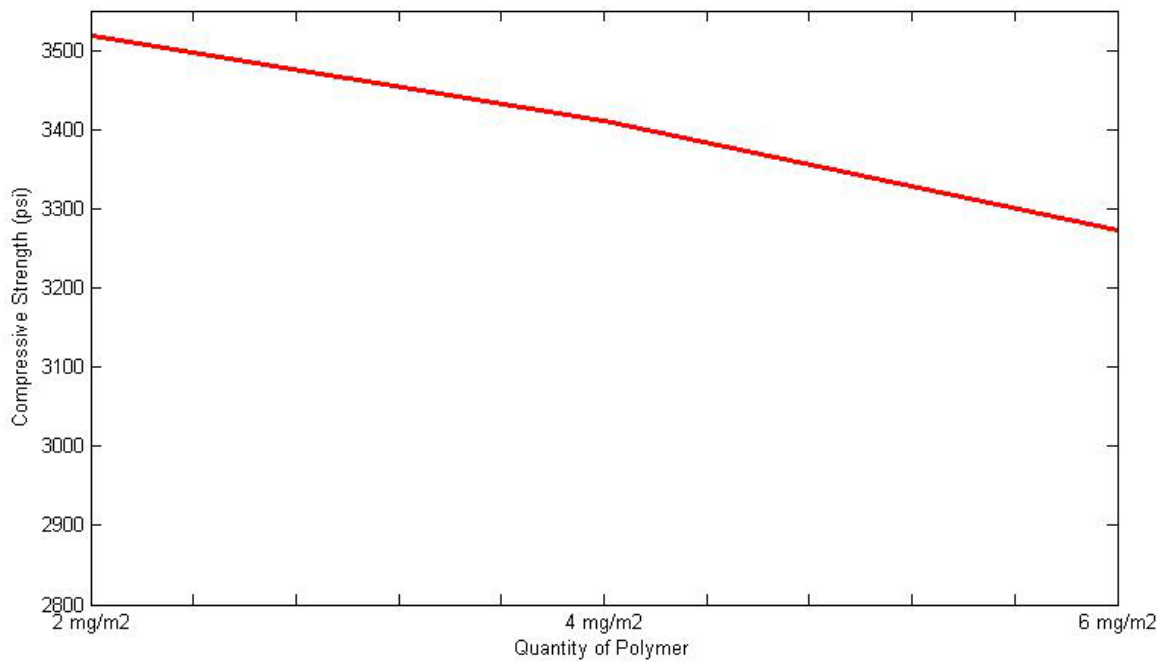


Figure 6 (b). Compressive strength vs quantity of poly (vinyl alcohol co-ethylene) - surface adsorbed

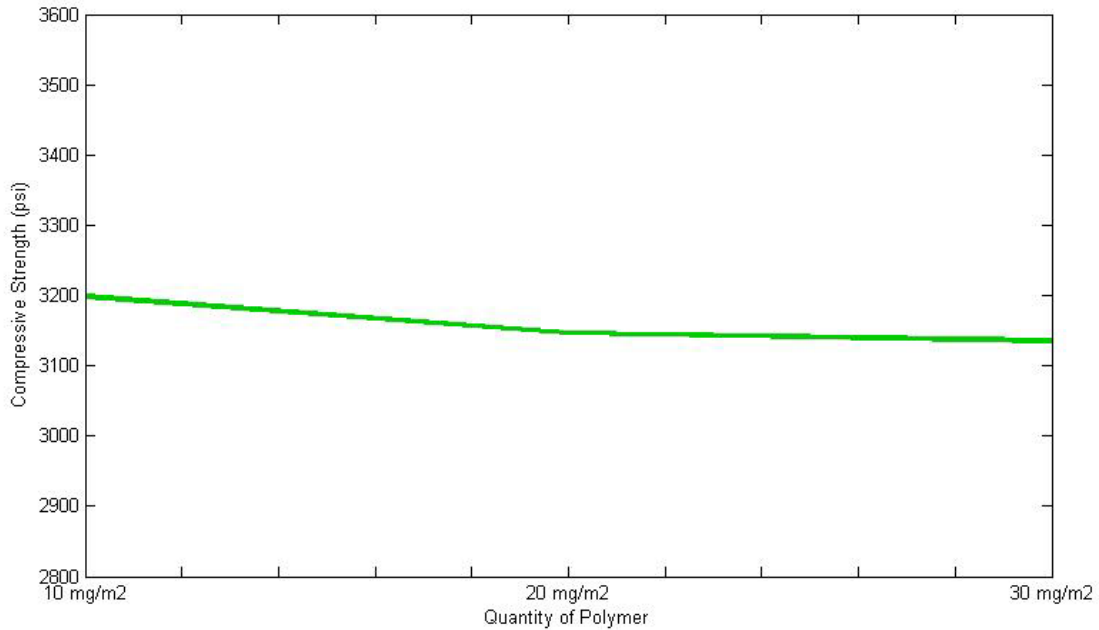


Figure 6 (c). Compressive strength vs quantity of poly (vinyl alcohol co-ethylene) – bulk

As seen from the results shown in table 3, the compressive strength of the pure concrete is higher than all the PMC types, apart from the pure resin samples, which has an extremely high value. Also the compressive strength reduces as the amount of polymer increases.

2. Flexure test

The prepared specimens were cured for 28 days each and were tested for flexure strength, according to ASTM C78, using the Tinius Olsen machine as shown in figure 7.



Fig. 7(a) Flexure sample before testing



Fig. 7(a) Flexure sample after testing

3 samples of each category as described in Table 4 were prepared and the stress at failure was measured.

Table 4. Polymer Quantity and Stress at failure for the respective samples.

Polymer	Quantity of Polymer	No of Samples	Stress at Failure (psi)
Pure Concrete	Nil	3	495
Polyurethane (PU)	50%	3	471
	100%	3	434
Poly (vinyl alcohol co-ethylene)	6 mg/m ²	3	509
	12 mg/m ²	3	556

Conclusion

The aim of this research was to get better quality of concrete in terms of compressive strength, by modifying interfacial transition zone (ITZ) by means of addition of polymers. However as discussed in the results, the compressive strength of the PMC is less than the pure concrete. This is attributed to the fact that in the samples with aggregate treated with PU, loses its porosity due to a layer of PU on the aggregate surface as PU is a known hydrophobic agent. A layer of PU on the aggregate surface results in the lack of hydration of aggregate and cement particles and leads to weaker ITZ. The addition of poly (vinyl alcohol co-ethylene) also proved not very useful. Though it is not a hydrophobic polymer, it formed a very fine layer on the surface of the aggregate but failed to facilitate that formation of stronger ITZ. The polymers investigated in this study (PU and poly (vinyl alcohol co-ethylene)) are not suitable for increasing the compressive strength. However, it was observed that for poly (vinyl alcohol co-ethylene), there is a substantial increase in the flexure strength.

Acknowledgment

This project is funded by National University Transportation Center (NUTC) at Missouri S&T. Support from Center for Infrastructure Engineering Studies is gratefully acknowledged. The authors would like to thank Amanda Steele for her help.

Publication

G. Dhaliwal, M. Mohamed, K. Chandrashekhara, T. Schuman, J. Volz, and K. Khayat, "Performance Evaluation of Polymer Modified Concrete using Polyurethane and Poly (vinyl alcohol co-ethylene)", Proceedings of the CAMX conference, Orlando, FL, October 13-16, 2014 (to appear)

References

1. Larbi, J.A. and Bijen, M.J.M.; "Bond Strength Development between Latex Modified Cement Paste and Steel"; *Cement and Concrete Research*, Vol. 17, pp. 562-571, 1988.
2. Larbi, J.A. and Bijen, M.J.M.; "Influence of Polymer Modification on the Hydration of Portland Cement"; *Cement and Concrete Research*, Vol. 21, pp. 242-250, 1990.
3. Lewis, W.J. and Lewis, G.; "The Influence of Polymer Latex Modifiers on the Properties of Concrete"; *Composites*, Vol. 21, Issue 6, pp. 487-494, 1990.
4. Colak, A.; "Properties of Plain and Latex Modified Portland Cement Pastes and Concretes With and Without Superplasticizer"; *Cement and Concrete Research*, Vol. 35, pp. 1510-1521, 2005.
5. Ukrainczyk, N. and Rogina, A.; "Styrene-Butadiene Latex Modified Calcium Aluminate Cement Mortar"; *Cement and Concrete Composites*, Vol. 41, pp. 16-23, 2013.
6. Scrivener, K.L. and Crumbie, A.K.; "The Interfacial Transition Zone (ITZ) between Cement Paste and Concrete"; *Interface Science*, Vol. 12, pp. 411-421, 2004.
7. Ion, I., Aguiar, J.B., Angelescu, N. and Stanciu, D.; "Properties of Polymer Modified Concrete in Fresh and Hardened State"; *Advanced Material Research*, Vol. 687, pp. 201-212, 2013.
8. Rao, G.A. and Prasad, R.; "Influence of Interface Properties on Fracture Behavior of Concrete"; *Sadhana*, Vol. 32, Part 2, pp. 193-208, 2011.
9. Gorninski, J.P. and Dal Molin, D.C.; "Comparative Assessment of Isophthalic and Orthophthalic Polyester Polymer Concrete"; *Construction and Building Materials*, Vol. 21, pp. 546-555, 2007.

10. Agavriloaie, L., Oprea, S., Barbuta, M. and Luca, M.; "Characterization of Polymer Concrete with Epoxy Polyurethane Acryl Matrix"; *Construction and Building Materials*, Vol. 31, pp. 190-196, 2012.
11. Isamail, M. and Muhammad, B.; "Performance of Natural Rubber Latex Modified Concrete in Acidic and Sulphated Environment"; *Construction and Building Materials*, Vol. 31, pp. 129-134, 2012.
12. Blum, F.D. and Lin, W.Y.; "Segmental Dynamics of Bulk and Adsorbed Poly (Methyl Acrylate) By Deuterium NMR: Effect of Adsorbed Amount"; *Macromolecules*, Vol. 30, pp. 5331-5338, 1997.
13. Blum, F.D. and Young, E.N.; "Thermal Analysis of Adsorbed Poly (Methyl Acrylate) on Silica"; *Langmuir*, Vol. 22, pp. 4741-4744, 2006.
14. Blum, F.D. and Porter, E.C.; "Thermal Characterization of Adsorbed Poly Styrene Using Modulated DSC"; *Macromolecules*, Vol. 35, pp. 7448-7452, 2002.
15. Blum, F.D. and Lin, W.Y.; "Dynamics of Adsorbed Poly (Methyl Acrylate) and Poly (Methyl Methacrylate) on Silica"; *Colloid Polymer Science*, Vol. 281, pp. 197-203, 2003.
16. Blum, F.D. and Porter, E.C.; "Thermal Characterization of PMMA Thin Films Using Modulated DSC"; *Macromolecules*, Vol. 33, pp. 7016-7020, 2000.

17.