The Significance of Nanoparticles on Bond Strength of Polymer Concrete to Steel

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Abstract

Polymer concrete (PC) is a commonly used material in construction due to its improved durability and good bond strength to steel substrate. PC has been suggested as a repair and seal material to restore the bond between the cement annulus and the steel casing in wells that penetrate formations under consideration for CO₂ sequestration. Nanoparticles including Multi-Walled Carbon Nano Tubes (MWCNTs), Aluminum Nanoparticles (ANPs) and Silica Nano particles (SNPs) were added to an epoxy-based PC to examine how the nanoparticles affect the bond strength of PC to a steel substrate. Slant shear tests were used to determine the bond strength of PC incorporating nanomaterials to steel; results reveal that PC incorporating nanomaterials has an improved bond strength to steel substrate compared with neat PC. In particular, ANPs improve the bond strength by 51% over neat PC. Local shear stresses, extracted from Finite Element (FE) analysis of the slant shear test, were found to be as much as twice the apparent/average shear/bond strength. These results suggest that the impact of nanomaterials is higher than that shown by the apparent strength. Fourier Transform Infrared (FTIR) measurements of epoxy with and without nanomaterials showed ANPs to influence curing of epoxy, which might explain the improved bond strength of PC incorporating ANPs.

Keywords: Polymer Concrete, Slant Shear Test, Bond Strength, Nanomaterials, Finite Element Analysis.

1. Introduction

Polymer Concrete (PC) is a commonly used material in construction and repair work for its high compressive strength, improved durability characteristics, high ductility, resistance to aggressive chemicals and superior bond strength to steel and concrete substrates compared with Portland cement concrete [1]. PC is made by mixing a thermoset polymer, e.g. epoxy, with aggregate as a filler. PC is preferred in bridge deck overlays for its improved abrasion resistance [1-2]. Recently, it was suggested that repair materials are needed to seal the interfacial cracks that often develop between steel casing and the cement annulus in wells in the vicinity of formations identified for CO₂ sequestration [3] as leaky wells are a critical issue for the implementation of carbon capture and storage. Such application requires PC to have superior bond strength to steel surfaces to accommodate harsh subterranean service conditions. The addition of nanomaterials was shown to improve mechanical properties of PC [4-5] and thus might enable its use to repair of damaged wells.

Polymer cement nanocomposites (PCN) are a class of polymer concrete where nanoparticles are dispersed in the polymer matrix prior to producing PC. Inclusion of nanoparticles introduces a significantly large number of particles within the matrix even at very low weight proportions [6]. Wetzel et al. [7] showed that the volume occupied by the addition of 3 microparticles corresponds to 3 million nanoparticles. The very small size and relatively high number of nanoparticles allow significant interaction between nanomaterials and the polymer matrix at the chemical as well as the physical level. Surface functionalized nanoparticles will thus alter the polymer chemistry producing a new type of PCN that may be significantly different than the original polymer matrix [8]. Surface functionalization of the nanoparticles is an important process for it enabling the nanoparticles to chemically react with the polymer matrix and produce a new polymer nanocomposite. However, in order to effectively disperse the nanoparticles within the matrix, high shear mixing and methods to prevent particle agglomeration such as ultra-sonication are often required [9].

Carbon Nanotubes (CNTs) are made from concentrically rolled single or multiple graphene sheets of nanoscale. CNTs possess exceptional strength, stiffness and failure strain as well as a very high aspect ratio [10]. The elastic modulus of CNTs reaches 1 TPa and tensile strength 100 GPa [11-12]. Uniformly dispersed CNTs improve the bond strength, elastic modulus and ultimate tensile strength of the composite [13]. Multi-walled carbon nanotubes (MWCNTs) represent one species of CNTs with similar or little lower mechanical

properties and much lower cost compared with CNTs. Alumina Nanoparticles (ANPs) are simply Aluminum Oxide (Al_2O_3) of nanoscale particles. The addition of ANPs was reported to increase the flexural modulus, toughness, glass transition temperature, resistance to fatigue crack propagation [14], tensile strength and durability [15]. Silica Nanoparticles (SNPs) are among the smallest size nanoparticles available. They are reported to improve the compressive strength, elastic moduli, fatigue strength [16], adhesion, and scratch and corrosion resistance [17]. The selection of the three nanoparticles (MWCNTs, ANPs, and SNPs) was based on prior efforts to improve adhesion and fracture toughness [13, 17, 18, 19].

Bond strength of polymers to substrates is developed due to physical and chemical bonds [20]. Chemical bonds are induced by chemical reaction of the polymer to the adhering substrate. Physical bonds are developed through Van Der Waal forces [21]. Inclusion of nanoparticles can enable a chemical interaction and/or generate new chemical bonds that would not be activated with the neat polymer. Bond strength tests include pull-off, twist-off [20], flexural [22] and slant shear tests [21, 22]. Pull-off test reports the most conservative bond strength among all tests as it provides the lowest bond strength values [19, 21-23]. Momayez et al. showed that Pull-off in comparison to slant shear, splitting prism and Bi-surface shear tests pull-off not is the most suitable for bond strength tests where tension is the dominant state of stress [19]. Tests like slant shear and Bi-surface shear impose a state of indirect tension by applying compression forces that result in shear stress over the bonded surface in question. However, the slant shear test is more suitable for examining vertical or inclined rather than horizontal bond surface. Two types of failure are associated with slant shear test; cohesive and adhesive failures. Cohesive failure takes place at the polymer side of the interface and correlates to a state of stress where the shear stress in the polymer exceeds the polymer's ultimate shear strength. Adhesive failure takes place at the bond interface between the two materials. Most standards suggest an angle of 60 degrees with the horizontal surface to favor adhesive failure to take place [22, 23]. Materials that possess significantly high compressive strength tend to experience adhesive failure when surface roughness and interface angle are carefully chosen [22]. ASTM standards suggest obtaining the average bond strength by dividing the vertical load by the slanted area of contact leading to what we denote as the apparent bond strength.

The objective of this study is to investigate the influence of incorporating nanomaterials in PC on the apparent bond strength of epoxy PC and steel. We also examine the significance of nanomaterials on the bond strength between PC and steel and the associated effect on the local shear stresses developed at the interface compared with the apparent bond strength. Experimental investigations are conducted to evaluate and explain the significance of nanomaterials on PC-steel bond strength. Finite element analysis is used to model slant shear tests to estimate local shear stresses that develop along the interface between the two materials

2. Experimental methods

Slant shear tests were carried out for neat PC and PC incorporating MWCNTs, ANPs and SNPs. Compression tests were also performed to extract the stress-strain response of PCs incorporating various nanomaterials.

2.1. Materials

Novolac epoxy system was selected for a potential well repair material principally due to its high chemical resistance. Novolac epoxy system (or HCE POLYAMINE) is a low viscosity cycloaliphatic polyamine blend with low viscosity hardener. Three types of nanoparticles were used: MWCNTs, SNPs, and ANPs. The MWCNTs were functionalized with carboxyl group (COOH) group with diameter of 20-30 nm and 10-30 μm length. The MWCNTs were produced using Catalyzed Chemical Vapor Deposition Technique (CCVD) by Cheap-Tubes. Functionalization was performed by the manufacturer by means of acid treatment chemistry of $\text{H}_2\text{SO}_4/\text{HNO}_3$. Carboxyl groups were attached at the ends and side walls of the nanotubes. This process is often performed by adding H_2O_2 to the chemical treatment as reported by Zhu et al. and Osorio et al [24, 25]. SNPs was AEREOSIL® 380 chemically prepared silicon dioxide powder produced by Evonik Degussa with an average particle size of 7 nm. ANPs are Aluminum Oxide Al_2O_3 with maximum particle size of 50 nm were obtained from Sigma Aldrich Inc. **Table 1** summarizes mixture proportions of polymer concrete. **Table 2** describes all of PCN mixtures and used denotations. We note that PC denotes neat polymer concrete mixes, PCNC denotes PC mixes with MWCNTs, PCNA denotes PC mixes with ANPs and PCNS denotes PC mixed with SNPs. The number following the mixture denotation represents the nanomaterials content in the mix represented as percentage of epoxy weight.

2.2. Specimen Preparation

The dispersion process of nanoparticles is accomplished by heating the epoxy resin to 110°C and magnetically stirring at 800 rpm. Nanomaterials were then added to the epoxy and dispersed using magnetic stirring for two hours. Next, the resin incorporating the nanomaterials was placed in a sonicator at 60°C for two hours. Ultra-sonication improves dispersion by generating microscopic bubbles within the resin that release energy and prevents particle agglomeration, thus leading to a uniform dispersion. Degassing using the sonicator hot bath option was performed to eliminate any air bubbles or voids within the matrix. The resin was then left to cool to room temperature for one hour. The hardener and the resin with dispersed nanoparticles were then mixed together to produce uniform polymer nanocomposite. Crystalline silica (quartz) and ceramic microspheres powder were then added as aggregate fillers to produce PCN mix. Curing was performed in room temperature for seven days. The dispersion technique was kept constant to avoid the difference associated with different processing techniques on the resultant polymer nanocomposite. MWCNTs proved to be more challenging to disperse than ANPs and SNPs due to their high aspect ratio and strong Van der Waals and Coulomb attraction forces. Hence, scanning electron microscope (SEM) images were collected for epoxy samples containing 2.0 wt.% MWCNTs in order to ensure proper dispersion at the highest content applied. **Fig. 1** shows the SEM images at two different locations of epoxy samples confirming no agglomeration achieving uniform dispersion of MWCNTs.

2.3. Slant shear test

Slant shear tests were used to measure the bond strength of PCN-steel substrates. The steel substrate surface was sandblasted to a minimum of 4.0 mil (0.1016 mm) clean. PCN was cast on the steel part at 60 degrees with the horizontal in two layers each compacted 25 times with the weight of standard concrete compaction rod. **Fig. 2** shows a schematic of the slant shear test as performed according to ASTM C882/C882M [26]. Five specimens of each PCN were tested. The alignment of PC to steel was also clarified through high resolution camera to ensure proper alignment and no slippage prior to testing as shown in **Fig. 3**. The apparent shear strength is given as

$$\tau = \frac{P \sin(60)}{A / \cos(60)} = \frac{P}{A} \sin(60) \cos(60) \quad (5)$$

Where P is vertical applied load and A is the cross-sectional area of the cylinder

2.4. Stress-strain behavior of PCN

Uniaxial compression testing of PCNs were performed using several longitudinal and lateral strains strain gages to extract the constitutive stress-strain relationship conforming with ASTM C469/C469M [27]. Five specimens of each PCN mixture were tested. The results of this test allowed determining the compressive strength, modulus of elasticity “ E ” and Poisson’s ratio (ν) of the PCN mixes as presented in Eq. 5 and 6, respectively.

$$E = \frac{\Delta\sigma}{\Delta\varepsilon_{VL}} \quad (6)$$

$$\nu = \frac{\Delta\varepsilon_{Lat}}{\Delta\varepsilon_{VL}} \quad (7)$$

where $\Delta\sigma$ is the change in vertical stress within linear region of the stress-strain relationship. $\Delta\varepsilon_{VL}$ is the corresponding change in vertical strain and $\Delta\varepsilon_{Lat}$ is the corresponding change in lateral strain within this specific change in stress $\Delta\sigma$.

2.5. Fourier Transform Infrared (FTIR) Analysis

To investigate the chemical effect of nanomaterials on PC and the significance of this effect on bond of PC with steel, Fourier Transform Infrared (FTIR) spectroscopy analysis was conducted. FTIR analysis was conducted on 25.4 mm $\times$ 25.4 mm epoxy specimen with and without the nanomaterials. Only the ratio of 1% of MWCNTs, SNPs, and ANPs were used for the FTIR analyses. Further FTIR analysis of SNPs incorporating 0.5, 1.0 and 2.0 SNPs was also performed to explain the significance of incorporating SNPs on epoxy. Specimens were prepared using the same method used to prepare PC. A PerkinElmer FTIR with Universal Attenuated Total Reflectance (UATR) accessories was used for the analysis. The spectra were recorded with a horizontal ATR accessory and a DiComp crystal (composed of a diamond ATR with a zinc selenide focusing element). 4000 scans were collected at a resolution of 4 cm^{-1} . The spectra were then converted to absorbance using the Kramers-Kronig equation for FTIR analysis [28].

3. Finite Element Analysis

Finite element analyses of the slant shear test configuration was conducted using ABAQUS modeling software. PCN was defined as a nonlinear elastic-plastic material using the constitutive stress-strain response measured in the uniaxial compression tests. The steel was assumed to be elastic perfectly plastic material. Convergence studies used two different types of built-in elements: 8-node linear hexagonal and 6-node linear triangular. These element types are capable of producing computationally inexpensive solutions for stress calculations. For each element type, different mesh sizes were used varying from 9,480 elements to 74,524 elements. Boundary conditions fixed the steel part from the bottom and prevented lateral deformation of the assembly. **Fig.4(a)** shows the boundary conditions as applied on the model. **Fig.4(c)** shows the meshed model using 6-node linear triangular elements. Displacement was applied to the top of PC to simulate slant shear tests. Load-displacement curves were extracted from the simulations and compared to those observed in the slant shear tests.

In order to define contact between PC and steel, a zero-thickness cohesive contact element was defined. Bilinear shear stress-slippage relationship was used to describe the contact element as shown in **Fig.4(b)** [29, 30]. This relationship is based on pure in-plane shear fracture mode (mode II) and is defined in ABAQUS using damage and cohesive behavior interaction [31]. The cohesive element characterizes the initial slope of the stress-slip curve (K_I) which is governed by the interfacial stiffness between the two slant shear test parts. The damage element on the other hand is prescribed using three components; initiation, evolution and stabilization. Firstly, damage initiation represents that maximum nominal stress in shear fracture mode (τ_u) characterized by the peak of the stress-slip curve. Secondly, damage evolution in this model was used based on the critical energy release rate in mode II (G_{II}) which denotes the area under the stress-slip curve. Finally, damage stabilization represents the energy dissipation module and is governed by the viscosity coefficient (V). In general, lower values of V signify rapid energy release and since failure in slant shear test is sudden, a constant low value of 0.001 was selected for all models. The values of τ_u , G_{II} , V and K_I were determined through experimental validation of the FE simulation and back-solving for those parameters [32]. This was performed using a trial and error for-loop where the values of the cohesive and damage model were estimated and the resultant load-displacement curve of the simulation was matched with the experimental. Sensitivity

analysis of the shear strength, critical energy release rate and interfacial stiffness were performed for the finite element model and values reported were proved to match well the experimental observations. Our objective is to use the validated FE model to realize the local shear stresses developed at failure of the slant shear test. **Table 3** summarizes the contact interaction properties. **Fig.5** shows load-displacement curves for both FE model and slant shear test for the selected mixes namely PC-Neat, PCNC-0.5, PCNA-0.5, PCNA-2.0, PCNS-0.5 and PCNS-2.0.

4. Results and Discussion

Apparent shear/bond strength results of slant shear tests of PCN and steel are shown in **Fig. 6**. All test specimens failed at the adhesion interface and no cohesive failure was observed as shown in **Fig.7**. As explained later interpreting the results of FEA, the samples failed when the fracture energy criteria G_{II} was reached. Hence, sudden failure was observed in the mechanical testing of slant shear where as FEA explored the critical location over the shear interface where the fracture criteria was satisfied. PCNs showed a significant increase in apparent bond strength compared with neat PC. Results of mixes incorporating MWCNTs at 0.5, 1.0 and 2.0 wt.% showed a similar increase of 7% in apparent bond strength compared with neat PC. This result suggests no advantage with respect to apparent bond strength by using MWCNTs beyond 0.5 wt.%. An increase in ANPs content corresponded to increase in apparent bond strength: apparent bond strengths of 20, 23 and 51% above neat PC with 0.5, 1.0 and 2.0 wt.% of added ANPs, respectively. This result may be attributed to the possible chemical reactions of ANPs with -OH groups formed on sand blasted steel surface leading to higher bond strength [21]. PC specimens incorporating NS showed an increase of 7 and 18% for 0.5 and 1.0 wt.% NS respectively and a significant drop of 41% at 2.0 wt.% content. The decrease in the apparent bond strength at high SNPs contents is attributed to its adverse effect on flowability. Thus, increasing the number of voids onto the PC-steel interface which weakens the bond. Furthermore, since SNPS are unable to interact with either the host matrix or steel. Increasing the content of SNPs hinders the reaction between the polymer matrix and steel as it occupies large unreacted surface area over the interface.

Fig.8 shows the stress-strain of the different PC with nanomaterials. In general, the incorporation of nanomaterials into PC resulted in a decrease in stiffness with the exception of PCNA-2.0. PC is highly ductile as proven by the large softening regions established post peak stress. Samples incorporating SNPS reached

the strength peak at significantly higher strain in comparison with all other samples. This is attributed to the improvement in shear stress transfer due to the high surface area of nanomaterials and improved packing density of polymeric chains. **Table 4** presents the calculated elastic modulus and Poisson's ratio for all PC mixes. The change in elastic modulus and Poisson's ratio is greatly affected by the chemical effect of nanoparticles on the host matrix which is further explained with the aid of FTIR observations. It is important to note that, with the proven effect of nanoparticles on the chemistry of epoxy based on the FTIR spectra, application of the rule of mixture to predict the mechanical properties of epoxy nanocomposites and thus PC is not possible. Further research is warranted to suggest alternative methods to classical rule of mixture that can account for the chemical effect of the nanoscale inclusions on the mechanical properties of the matrix.

All PCs had an increased Poisson's ratio compared with neat PC. FE results showed significantly higher values of maximum local shear stresses compared with the apparent shear strength. **Fig.9** compares the apparent shear strength and the maximum local shear stresses. An increase in the maximum local shear stress of 88, 107, 115, 125, 130, and 166% can be observed for PCNA-0.5, PCNS-2.0, PCNA-2.0, PCNC-0.5, PC-Neat, and PCNS-0.5 respectively. The difference between the apparent/average shear strength and the maximum local shear stress can be attributed to the difference in elastic modulus of PC with and without nanomaterials and steel. Further research is warranted to separate the effect of difference in elastic modulus of PC and steel substrate from the changes in shear strength. Nevertheless, the trend of increasing the shear/bond strength by incorporating nanomaterials can still be observed. There is no obvious relationship between the difference in stiffness between PC incorporating nanomaterials and the difference between apparent shear strength and maximum local shear stress at the interface. This might be attributed to the fact that the apparent shear strength is dependent on the mechanics of the test and the adhesion between PC and steel, which is affected by potential chemical reaction between the nanomaterials and epoxy in PC. Separation of these two effects seems difficult. FTIR analysis described below sheds light on potential chemical reaction of nanoparticles with epoxy and its potential effect of epoxy and PC moduli.

Further analysis of the FE simulation results shows strong correlation between Poisson's ratio and the shear modulus G described as $G = \frac{E}{2(1+\nu)}$ and the maximum local shear stresses at the interface. Since

allnanomaterials caused an increase in Poisson's ratio, the maximum local shear stress is decreased by the increase in Poisson's ratio. This analysis supports the results for PCNC-0.5 and PCNA-0.5 in comparison with neat PC. Furthermore, another important factor controlling the maximum local shear stresses is the shear contact stiffness K_t . The shear contact stiffness controls the slippage occurring at the interface (see **Fig. 4**) and may correspond to the friction between the contact surfaces. The effect of the shear contact stiffness on local shear stresses is apparent in the case of SNPs. FTIR analysis, discussed below, confirms that SNPs affected epoxy curing but acted as an inert filler. This might explain its ability to increase interface friction compared with MWCNTs or ANPs, which apparently have the ability to chemically react with the epoxy matrix and/or the steel surface.

Finally, FE analysis results were also used to examine the interfacial shear stress contours at the PC-steel interface. **Fig. 9** shows the load-displacement of neat PC extracted from the FE model with magnified slippage in the assembly at vertical displacements of 0.720 mm, 0.802 mm, and 0.837 mm. At each of these points, shear contours on the interface were plotted showing the maximum local shear stress to reach 40 MPa. Locations of maximum local shear stress concentration on the interface are shown in **Fig. 10**. Maximum local shear stress only develops at the location of minimum height of PC before reaching ultimate load as shown in **Fig. 10** and **Fig. 11(a)**. As slippage occurs, the maximum local shear stress moves along the interface. The maximum local shear stress path follows the height of PC from minimum to maximum as shown in transition in **Fig. 11** from (a), (b) and (c). Slant shear tests show that complete slippage occurs after the ultimate load due to release of energy as a result of bond failure.

Nonetheless, incorporating nanoparticles in PC resulted in increasing the bond strength of PC to steel substrates. This improvement in bond strength when measured in terms of maximum local shear stresses is less significant than that measured using the apparent shear strength. FE analysis showed that the increase of bond strength in terms of maximum local shear stress is 5, 23 and 42% for PCNC-0.5, PCNS-0.5, and PCNA-2.0 respectively and a decrease of 2 and 47% for PCNA-0.5 PCNS-2.0 when compared with neat PC. These values are lower than those improvements depicted by the apparent/average shear strength shown in **Fig. 6**. The analysis demonstrates that the simplistic approach of averaging the shear stress is insufficient to compare materials with significant different mechanical properties (e.g. elastic modulus and Poisson's ratio). It is

obvious that using slant shear test results to compare bond strength of materials with significantly different mechanical properties should be done with care and its results might better be interpreted using the finite element method.

FTIR spectrographs for neat epoxy and epoxy incorporating 1% MWCNTs, SNPs, and ANPs are shown in **Fig. 12**. FTIR spectra of MWCNTs/epoxy and SNPs/epoxy, show the traditional band of epoxy where absorption bands corresponding to O-H groups appeared at ($\sim 3200\text{--}3600\text{cm}^{-1}$), C-H band ($2850\text{--}2930\text{cm}^{-1}$), N-H band of primary amines ($1590\text{--}1615\text{cm}^{-1}$), C-N ($1030\text{--}1115\text{cm}^{-1}$), ether ($\sim 1230\text{cm}^{-1}$) and epoxide ring ($\sim 830\text{cm}^{-1}$), are all apparent and have similar relative ratios to the neat epoxy. However, the spectra of ANPs/epoxy look very different showing relatively higher ratios of epoxy ring, O-H band and primary N-H band intensities than the neat spectra. This may be attributed to the effect of nanoparticles on the curing behavior of the epoxy matrix. The curing reaction of the epoxy resin proceeds through the amines presented in the polyamide curing agent. The general illustrations of the chemical structures of the epoxy resin (Novolac epoxy-HCR Polyamine) and the possible reactions among its curing process follow Golru et al. [33]. Based on the curing mechanism and the results obtained from FTIR analysis, it can be concluded that the curing reaction was affected by the presence of ANPs. This can be understood from the greater peaks intensities of the epoxy ring ($\sim 830\text{cm}^{-1}$) and O-H groups ($\sim 3350\text{cm}^{-1}$) for the epoxy-ANPs nanocomposite compared with the neat sample. This is attributed to the effect of ANPs on epoxy curing reaction producing cured epoxy matrix having un-reacted functional groups; the source of effective bonding with steel surface.

The difference in the epoxy-ANPs nanocomposite can be explained by the fact that ANPs are known as an amphoteric substance meaning it can react with both acids and bases which allows it to act as an acid with a base and a base with an acid. ANPs, thus, reduce the epoxy curing reaction and consequently leave a relatively large amount of the epoxy resin groups (such as the epoxide ring, N-H band of primary amines, O-H groups) unreacted and available. This is represented by the significant increase in the epoxide ring, O-H and primary N-H band intensity in the FTIR spectra. This role of ANPs results in increasing the epoxy's chance to react with the sand blasted steel surface and thus improve the adhesion strength between PC and steel. The ability of ANPs to reduce epoxy curing was reported in the literature by Golru et al. [33] and Kadar et al. [34]. The increase in ANPs content would be expected to further increase the amount of unreacted epoxy

groups and consequently the adhesion strength. This explains the significant increase in bond strength (+51%) observed with 2.0% ANPs compared with neat epoxy. It might be important to note that in addition to the chemical effect, ANPs also worked as solid nanofiller and thus enabled increase of epoxy/PC stiffness at high content of 2.0% compared with neat PC. The final improved bond strength is apparently due to the combined effects of ANPs on the adhesion strength and the stiffness difference between PC and steel.

The above FTIR spectra also show that MWCNTs with its COOH functionalization resulted in esterification reaction with epoxy and produced the ester and amide peaks appearing at 1740 cm^{-1} and 1665 cm^{-1} , respectively. However, the low content of COOH functionalizing in MWCNTs makes this reaction ineffective due to the fact that curing of Novolac epoxy results in similar chemical groups. This similarity is shown in the inset in **Fig. 12**. This explains why the MWCNTs were not able to make significant improvement in adhesion strength between epoxy and steel. Finally, SNPs seem able to broaden the OH-band at $3200\text{--}3600\text{ cm}^{-1}$. To further investigate the effect of SNPs on epoxy curing, FTIR spectra of epoxy incorporating 0.5, 1.0 and 2.0% of SNPs, shown in **Fig. 13**, were further investigated.

It could be observed in **Fig. 13** that the hydroxyl absorption peak at 3410 cm^{-1} gets further broadening as SNPs content increased. This can be attributed to the effect of SNPs on the curing process of epoxy through phase separation and re-arranging of the hydroxyl groups [35]. The broad band region at about $3200\text{--}3600\text{ cm}^{-1}$ reflects the hydroxyl stretching vibration with multi-modes of inter- and intramolecular hydrogen bonds and represents combined effects of hydrogen bond in hydroxyl, hydroxyl/carbonyl groups and in water molecules [36, 37]. The FTIR spectra shows that incorporating SNPs in the epoxy matrix reduced its network formation process via lowering the crosslinking bonds and consequently changed the ratios of hydrogen bond modes which led to different geometry with different force constants and consequently broadening the absorption peak.

It is interesting to note that the effect of SNPs on adhesion was opposite to that of ANPs in spite of the fact that both nanomaterials affected epoxy curing. While both ANPs and SNPs resulted in steric hindrance effect that decreased the reactivity between the epoxy functional groups and the hardener, SNPs did not result in improving adhesion. This can be explained by the fact that the amphoteric and polar nature of ANPs enabled the remaining epoxy and OH groups to bond to steel surface. On the contrary, SNPs caused a shielding barrier

in the cured epoxy matrix due to their unreactive nature that prevented utilization of the active epoxy sites and thus did not improve the bond strength of polymer concrete and steel. The unreactive nature of fumed silica and silica nanoparticles and their need to surface functionalization when used with polymers has been reported in the literature [38-40]. The above study sheds light on the significance of nanoparticles on changing epoxy curing and the result such changes can make in altering bond of polymer concrete made with these epoxy-nanocomposites with steel.

5. Conclusions

This paper examines the bond strength of PC incorporating nanomaterials to steel substrates. The slant shear tests revealed that incorporating nanoparticles can improve the apparent bond strength between PCs and steel by up to 51% compared with neat PC. The best improvement in bond strength was achieved by 2.0% wt of alumina nanoparticles, which was the maximum amount used in this study. MWCNTs showed very limited to no increase in the bond strength with no improvement beyond 0.5 wt.%. SNPs showed a general decrease in bond strength compared to neat PC. The ability of alumina nanoparticles to improve bond strength of epoxy PC and steel might be attributed to potential chemical reaction of alumina and -OH groups formed on the sand blasted steel surface. The adverse effect of SNPs might be attributed to its inability to chemically react with Novolac epoxy making it to act as an inert filler only increasing friction at the steel interface.

Examining the constitutive stress-strain relation of PC incorporating nanomaterials showed a general decrease in stiffness and increase in Poisson's ratio. The drop in elastic modulus of PC incorporating nanomaterials compared with neat PC, the change in Poisson's ratio along with difference in contact shear stiffness result in a significant difference between the maximum local shear stress occurring at the interface and the apparent/average shear strength. This difference ranged from 88 to 166%. Considering the maximum local shear stresses developed at the interface, the significance of nanomaterials on the bond strength of PC to steel seems lower than that from the apparent bond strength determined from the slant shear test standard. Local shear stresses calculated from the finite element method confirmed that maximum local shear stress occurs at the area of minimum PC height and moves towards increasing PC height during the slant shear test. This analysis confirmed that there is a strong correlation between changes in Poisson's ratio and difference

between apparent shear strength and the maximum local shear stress. It is concluded that special care should be considered when interpreting slant shear test results to compare bond strength of materials with significantly different mechanical properties. Finally, FTIR analysis showed that ANPs resulted in significant reduction of epoxy curing and thus enabled further epoxy groups to react with the steel surface improving the adhesion strength between PC and steel. FTIR spectra also showed SNPs to alter epoxy curing. However, the unreactive nature of SNPs resulted in shielding barrier and prevented improving bond strength of polymer concrete incorporating SNPs with steel. FTIR observations might explain why ANPs were capable to significantly improve the bond strength of PC with steel compared with all other nanoparticles.

5. Acknowledgements

This material is based upon work supported by the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) under Grant Number DEFE0009562. This project is managed and administered by the DOE/NETL Storage Division and funded by DOE/NETL and cost-sharing partners. This paper was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof. The authors like to extend their thanks to Epoxy Chemicals Inc. and Transpo Industries Inc. for donating epoxy materials to the project. The authors also extend their thanks to PhD candidate Amina Mannan (UNM) for her continuous help in conducting and analysis of FTIR.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND2015-11102 J

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Figure Captions:

Fig.1: SEM images of epoxy samples containing 2.0 wt.% MWCNTs showing proper dispersion of nanotubes.

Fig.2: Slant shear test (left) schematics showing slant shear angle (right) actual specimen showing steel substrate and PC.

Fig.3: Vertical alignment using high resolution camera of PC and steel prior to slant shear testing.

Fig.4: FE model using ABAQUS simulation environment: (a) Boundary conditions (b) Bilinear shear stress-slip relation where K_t is shear contact stiffness, G_{II} is mode II fracture energy and τ_u is maximum shear stress (c) Meshed model using 74,524 elements.

Fig.5: Load-displacement curves of PC with different nanomaterials as measured experimentally during slant shear test and extracted using the finite element method for (a) PC-Neat, (b) PCNC-0.5, (c) PCNA-0.5, (d) PCNA-2.0, (e) PCNS-0.5, and (f) PCNS-2.0.

Fig.6: Apparent shear strength determined as average stress from slant shear tests for all PCNs. % difference shown depicts the difference between the PC with nanomaterials and neat PC shown in first column.

Fig.7: Slant shear fracture surface post-failure for PCNC, PCNS and PCNA showing complete adhesion failure.

Fig.8: Stress-strain relation for different PC incorporating different nanomaterials. Graphs of PC-Neat, PCNC-0.5, PCNA-0.5, PCNA-2.0, PCNS-0.5, and PCNS-2.0. Table show the extracted values for elastic modulus and Poisson's ratio for the different PC mixes.

Fig.8: Stress-strain relation for different PC incorporating different nanomaterials. Graphs of PC-Neat, PCNC-0.5, PCNA-0.5, PCNA-2.0, PCNS-0.5, and PCNS-2.0.

Fig.9: Shear strength for different PC incorporating nanomaterials interpreted using apparent shear strength (average stress based on slant shear standard) and maximum local shear stress using the finite element model. The % difference shown is the difference between the two values for different PC mix.

Fig.10: Load-displacement extract from finite element analysis of neat PC showing magnified slippage at 0.720mm, 0.802mm, and 0.837mm.

Fig.11: Shear contours showing locations of maximum local shear stress during slippage at vertical slip of (a) 0.720 mm (b) 0.802 mm and (c) 0.837 mm.

Fig.12: FTIR spectra of neat epoxy and epoxy incorporating 1.0 % ANPs, MWCNTs and SNPs showing the main epoxy groups and the significant changes appearing in the spectra using ANPs compared to the other two nanomaterials. The spectra also show a potential broadening of the OH band at 3200-3600 cm^{-1} due to SNPs. The spectra show the significant increase in the epoxy peaks with respect to base spectra in the case of ANPs compared to neat epoxy.

Fig.13: FTIR spectra of neat epoxy and epoxy incorporating 0.5, 1.0 and 2.0 % SNPs showing the significant band broadening of OH group at 3410 cm^{-1} due to incorporating SNPs.

Table Captions:

Table 1: PCN mix proportions

Table 2: Nanoparticles and their % weight of epoxy for the different PCN mixes

Table 3: Interface interaction properties as defined in ABAQUS.

Table 4: Elastic modulus and Poisson's ratio for the different PC incorporating nanomaterials

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Table 1: PCN mix proportions (kg/m³)

Epoxy resin	221
Epoxy hardener	96
Silica particle fillers	1200
Nanomaterial	wt. % of epoxy resin

Table 2: Nanoparticles and their % weight of epoxy for the different PCN mixes

PCN	Nanoparticles	% weight of epoxy
PC-Neat	None	0%
PCNC-0.5	MWCNTs	0.5%
PCNC-1.0		1.0%
PCNC-2.0		2.0%
PCNA-0.5	ANPs	0.5%
PCNA-1.0		1.0%
PCNA-2.0		2.0%
PCNS-0.5	SNPs	0.5%
PCNS-1.0		1.0%
PCNS-2.0		2.0%

Table 3: Interface interaction properties as defined in ABAQUS.

Contact Property	Damage			Cohesive Behavior
	Initiation	Evolution	Stabilization	
	Maximum shear stress (τ_u), MPa	Fracture energy (G_{II}), N/mm	Viscosity Coefficient (V)	Shear contact stiffness (K_t), MPa/mm
Mix				
PC-Neat	43	19	0.001	56
PCNC-0.5	45	29		46
PCNA-0.5	42	17		75
PCNA-2.0	61	24		92
PCNS-0.5	53	21		90
PCNS-2.0	23	37		12

Table 4: Elastic modulus and Poisson's ratio for the different PC incorporating nanomaterials.(Values presented are mean $\pm$ standard deviation.)

	PC-Neat	PCNC-0.5	PCNA-0.5	PCNA-2.0	PCNS-0.5	PCNS-2.0
Elastic modulus (GPa)	14.29 ± 2.19	10.30 ± 0.44	8.74 ± 0.23	15.09 ± 1.00	6.23 ± 0.25	3.76 ± 0.12
Poisson's ratio	0.22 ± 0.10	0.36 ± 0.02	0.37 ± 0.02	0.37 ± 0.07	0.36 ± 0.01	0.35 ± 0.05