A new polymer nanocomposite repair material for restoring wellbore seal integrity

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Abstract

Seal integrity of functional oil wells and abandoned wellbores used for CO₂ subsequent storage has become of significant interest with the oil and gas leaks worldwide. This is attributed to the fact that wellbores intersecting geographical formations contain potential leakage pathways. One of the critical leakage pathways is the cement-shale interface. In this paper, we examine the efficiency of a new polymer nanocomposite repair material that can be injected for sealing micro annulus in wellbores. The bond strength and microstructure of the interface of Type G oil well cement (reference), microfine cement, Novolac epoxy incorporating Neat, 0.25%, 0.5%, and 1.0% Aluminum Nanoparticles (ANPs) with shale is investigated. Interfacial bond strength testing shows that injected microfine cement repair has considerably low bond strength, while ANPs-epoxy nanocomposites have a bond strength that is an order of magnitude higher than cement. Microscopic investigations of the interface show that micro annulus interfacial cracks with widths up to 40 µm were observed at the cement-shale interface while these cracks were absent at the cement-epoxy-shale interface. Fourier Transform Infrared and Dynamic mechanical analysis measurements showed that ANPs improve interfacial bond by limiting epoxy crosslinking, and therefore allowing epoxy to form robust bonds with cement and shale.

Keywords: Seal, Wellbore Integrity, Micro annulus, Nanocomposites, Nanoalumina.

1. Introduction

Seal integrity of both production wells and abandoned wells is critical to a variety of subsurface applications, including geologic storage of CO₂. Loss of zonal isolation is a serious issue and is integral to ensuring protection of human health and the environment. Wellbores intersecting geological formations contain potential leakage pathways that exist due to either well-completion process or degradation of the cement and steel casing (Zhang and Bachu, 2011). Among the potential leakage pathways in wellbores as summarized schematically in Fig. 1 (Celia et al, 2005), the steel-cement and rock-cement interfaces are two of the most critical leakage pathways (Carey et al., 2007). While considerable attention has been given to the steel-cement interface (Baldan, 2004; Nakayama and Beaudoin, 1987; Zhai et al., 2006), little effort has been focused on studying the rock-cement interface. This article focuses on repair of the rock-, specifically shale, cement interface for seal integrity. Due to their low permeability, shale layers often serve as cap rocks for underlying hydrocarbon reservoirs. Ensuring the integrity of wellbores at locations where they penetrate these layers is important for the containment and control of reservoir fluids.

Fig. 1. Schematic representation of zonal isolation and potential leakage pathways (Celia et al., 2005).

Prior investigations have shown that the cement-shale bond is affected by both cement and shale. Cement shrinkage and growth of the calcium hydroxide crystals at the interfacial zone of cement-bonded surfaces are well-known reasons to weaken cement bond with most interfaces including the cement-shale interface

(Nakayama and Beaudoin, 1987; Mehta and Monteiro, 2013). Moreover, the swelling coefficient of the shale formation has a significant impact on interfacial bond between the cement and shale. The higher the swelling coefficient, the weaker the bond-strength is between the cement and shale (Ladvá et al., 2005). The morphology of the rock surface also significantly affects the bond strength of the cement-shale interface. Shale formation with higher surface roughness would tend to have higher bond strength with cement compared with smooth shale formations (Nasir and Fall, 2008). The presence of carbonated brine can significantly deteriorate cement and affect the wellbore seal integrity (Carey et al, 2007; Duguid and Scherer, 2010; Huet et al, 2010; Kutchko et al, 2077; Kutchko et al, 2008; Liteanu et al., 2009; Matteo and Scherer, 2012; Rimmelé et al, 2008). The above factors favor debonding between cement and shale over the long-term.

Repair of the cement-shale bond requires injecting a repair material that can fill the interfacial contact and improve seal integrity. A repair material should have a relatively low viscosity so it can flow during injection to penetrate microannulus cracks (micro cracks along a cement-shale contact interface). Such material should have minimal shrinkage to reduce the likelihood that a new flow path will develop between the repair material and the cement and/or shale. Furthermore, the repair material should also be flexible to prevent debonding due to further cement shrinkage, shale swelling, temperature changes and/or shock waves.

We suggest that polymer based materials are optimal repair materials to achieve these requirements. Polymers have shown very high bond strength with metallic surfaces (Baldan, 2004). Thermoset polymers, specifically Novolac-based epoxies, show very high bond strength with different surfaces. Moreover, incorporating nanomaterials such as Aluminum Nanoparticles (ANPs) in polymers was able to improve their mechanical properties and durability (Pocius, 2012; Salemi and Behfarnia, 2013; Shokrieh et al., 2012; Wetzel et al., 2006). Zhai et al., (2006) reported improved bond between polymer matrices and metallic surfaces when nanomaterials were dispersed in the polymer matrix. Our prior investigations showed that Novolac epoxy incorporating ANPs significantly improved the bond strength of the cement-steel interface (Genedy et al., 2014).

In this study, we investigate the efficiency of using Novolac epoxy incorporating ANPs as a repair material for sealing cement-shale microannulus. The bond strength of ANPs-epoxy nanocomposites incorporating different content of ANPs is investigated using push-out tests. In these tests, ANPs-epoxy nanocomposites were injected into an 800 μm artificial gap created between an inner shale cylinder and an outer cured cement socket. The ANPs-epoxy nanocomposites were compared to a standard microfine cement repair material, typically used in the industry, which was injected to fill the same above gap. The bond strengths of ANPs-epoxy polymer nanocomposites as well as the microfine cement repair materials were compared with the bond strength of a reference case where Type-G oil well cement (OWC) was cast around shale and fully cured to achieve the highest possible bond strength. Microstructural analysis including Dynamic Mechanical Analysis (DMA) and Fourier Transform Infrared (FTIR) analysis as well as light microscope investigations were conducted to understand the significance of nanomaterials on epoxy behavior.

2. Experimental methods

2.1. Materials

The shale used in this investigation was Mancos Shale. Type G (API Class G) OWC was used as the reference cement material. Microfine cement, generally used to repair cracks in oil wells, provided by the manufacturer was used. The microfine cement has a composition that is comparable to high sulfate-resistant cements and grain size (d_{95}) of 9.5 μm . The mix used for the microfine cement has water to cement ratio (w/c) of 0.7 and 2.0% of the dry cement weight super plasticizer (recommended by the manufacturer). Novolac epoxy was selected as the repair material due to its high chemical resistance, relatively high thermal performance and good flowability. Novolac epoxy system is a low viscosity cycloaliphatic polyamine blend with low viscosity hardener. Researchers showed water, acids (such as carbonated water) and saline solutions to have negligible effect on hardened Novolac epoxy (Atta et al. 2008, Tchoquessi Doidjo et al. 2013, Soares-Pozzi et al. 2016). ANPs were used to modify the epoxy matrix. ANPs are Aluminum Oxide Al_2O_3 with maximum particle size of 50 nm were obtained from Sigma Aldrich, Inc. Microscopic image of ANPs using transmission electron microscope (TEM) is shown in Fig. 2. Three weight contents of ANPs were examined in addition to neat epoxy being 0.25%, 0.50% and 1.0% by weight of the epoxy resin.

2.2. Polymer nanocomposite preparation

To prepare the polymer nanocomposite, the ANPs were added to the required amount of the resin, and the mix was stirred for 2 hours at 110 °C using magnetic stirring. This relatively high mixing temperature was used to reduce the resin viscosity and improve the dispersion of ANPs. The mix was then sonicated for 2 additional hours at 65 °C using an ultrasonic homogenizer. The polymer resin nanocomposite was left to cool and reach room temperature and then mixed with the hardener with mixing ratio 2.2:1 (Resin: Hardener) for 3 minutes using low speed mixer until a uniform mix was obtained. It is important that the nanomaterials are very well dispersed in the mixture to prevent gravity settling. This was achieved by the interaction of ANPs with the polar groups of the epoxy resin.

Fig. 2. TEM micrograph showing aluminum nanoparticles and their size.

2.3. Viscosity of repair materials

Viscosity test was conducted using rotational Viscometer following AASHTO T316 (AASHTO, 2013). The viscosity was measured for all material at room temperature (22 °C). SC4-21 needle spindles, rotating at 20 rpm, were used for viscosity measurements. The spindles were allowed to rotate for 1 minute, after which three readings were taken at 15-second intervals. The test was performed as per the AASHTO standard.

2.4. Interfacial bond strength testing (Push-out test)

Two sets of specimens were prepared for push-out tests (Fig. 3). The first set was used to measure the bond strength between the shale and Type G cement. A shale core of 25.4 mm diameter and a length greater than 30 mm was fixed in the center of a steel cylinder with an outer diameter of 100 mm and thickness of 3.2 mm;

cement paste was then cast around the shale to produce cylindrical specimens with a diameter of 101.4 mm and height of 50.8 mm. The second set of specimens was prepared to investigate the bond strength of the repair materials injected in an artificial microannulus between cement and shale. Hollow Type G cement cylindrical specimens confined with steel cylinders with inner diameter of 27 mm, total outer diameter of 101.4 mm and height of 50.8 mm were cast first. These specimens were cured at 100% humidity environment at room temperature for 28 days. After the cement cylinder was cured, the shale core with a diameter of 25.4 mm was placed in the center of the hole, which produced a gap or microannulus between the cement and shale of nominally 800 μm . Repair material was then supplied along the top shale-cement contact and allowed to flow by gravity into the microannulus (Fig. 4). The repair material was added into the crack until the repair material no longer flowed into the crack. Five repair materials were tested in this investigation: standard microfine cement, Novolac epoxy, and Novolac epoxy with 3 different contents of ANPs (0.25 wt.%, 0.5 wt.%, and 1.0 w.%). ANPs were added as a weight percentage of the epoxy total weight.

Fig. 3. Schematic of the push-out test specimens for (a) first set of specimens and (b) second set of specimens.

Fig. 4. Placing repair material at the cement-shale microannulus.

All specimens were tested at age 7 days after repair (or curing for reference specimens). Cement specimens were cured in 100% humidity while polymer nanocomposites specimens were air cured at room temperature.

The push-out test setup is shown in Fig. 5. The push-out test was conducted under two-stage displacement control protocol. The test started with a rate of 0.1 mm/min for the first 5 mm, after which the loading rate was increased to 1.0 mm/min. Test load and displacement were recorded using sampling rate of 1 Hz. The initial lower displacement rate allowed bond failure to take place at low strain rate. The greater displacement rate post-peak reduced the total test time to about 1 hour. The bond strength was calculated using Equation (1).

$$\tau = \frac{P}{\pi DL} \quad (1)$$

where τ is the interfacial bond strength, P is the peak load, D is the diameter of the shale core of 25.4 mm, and L is the embedment length of 25.4 mm.

Fig. 5. Push-out test setup.

2.5. Microstructure investigations

Microstructure investigations were conducted to gain insight into the bond strength developed in the repaired systems. The effect of ANPs on epoxy matrix was examined using FTIR Analysis and DMA. Microscopic images of the shale-cement interface with the different repair materials were also examined.

2.5.1. Fourier Transform Infrared (FTIR) Analysis

FTIR analysis was conducted on the polymer specimen with (1%) and without ANPs. A PerkinElmer FTIR with the Universal Attenuated Total Reflectance (UATR) accessory 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). For each sample, 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 (Griffiths and de Hasseth, 2007).

2.5.2. Dynamic Mechanical Analyses (DMA)

The effect of ANPs on crosslinking of epoxy was investigated using DMA. The crosslinking density was determined by applying the theory of rubbery elasticity (Hill, 1997) using Equation (2).

$$v_e = \frac{E'}{3RT} \quad (2)$$

v_e is the crosslinking density, E' is storage modulus in the rubbery plateau, T is the temperature in Kelvin corresponding to the storage modulus value, and R is Gas Constant. The rubbery plateau was considered to be at temperature $50\text{ }^{\circ}\text{C}$ above glass transition temperature T_g (Lee and Yee, 2000). The storage modulus at rubbery plateau was measured using DMA Q800. The molecular weight between crosslinks can be calculated using Equation (3).

$$M_c = \frac{\rho}{v_e} \quad (3)$$

where M_c is molecular weight between crosslinks and ρ is the density of the polymer nanocomposite. As the crosslinking of a polymer resin increases when the molecular weight between crosslinks decreases (Lee and Yee, 2000; Liang and Pearson, 2009), A measure for the degree of crosslinking X_{link} is suggested here as an inverse for the molecular weight between crosslinks in a unit volume as in Equation (4).

$$X_{link} = \frac{1}{M_c} = \frac{v_e}{\rho} \quad (4)$$

where X_{link} is a measure of the degree of crosslinking of the polymer nanocomposite.

2.6. Microscopic investigation

Light microscopes with two different levels of magnification (100X and 500X) were used to observe the shale-cement interface with the different repair materials.

3. Results and Discussion

Median load-displacement curves of specimens with different repair materials are shown in Fig. 6. It is obvious that microfine cement as repair material has a very low shear capacity and very low energy absorption (represented by the area under the curve) compared with all the epoxy nanocomposite repair materials. Compared to neat epoxy, the nanocomposite with 0.25% ANPs does not appear to have increased shear capacity or energy absorption. However, it is apparent that adding 0.5 % ANPs to the epoxy improved both the shear capacity and its energy absorption significantly; little additional benefit appears to be gained by increasing the ANP to 1.0%. Fig.6 also shows that the peak displacement for epoxy incorporating ANPs were in the order of 5.0 mm for neat epoxy and epoxy incorporating 0.25% ANPs compared with 3.0 mm for epoxy incorporating 0.5 and 1.0% ANPs compared to 0.7 mm for microfine cement. A very sharp decrease in load carrying capacity was observed for microfine cement compared with a much more gradual decrease observed for epoxy nanocomposites.

Fig. 6. Median load-displacement curves of specimens repaired with microfine cement and epoxy-based materials.

Fig. 7 shows the bond strength of the reference case (cement case around shale) and all repair materials. Table.1 presents the bond strength for all repair materials compared with reference case. With all failures taking place at the shale epoxy interface, shear effect on epoxy was ignored. Statistical analysis using student t-test with 95% level of confidence shows that the reduction of bond strength of microfine cement was statistically insignificant. However, the increase in the bond strength of all ANPS-epoxy nanocomposites is statistically significant when compared with the reference case or the microfine repair cement.

Table.1: Bond strength of repair material compared with reference case.

Material	Reference	Microfine cement	Neat Epoxy	0.25% ANPs	0.5% ANPs	1.0% ANPs
Bond Strength [MPa]	4.5±0.1	3.5±0.8	12.3±0.9	12.6±0.1	15.4±0.3	15.9±0.9

Fig. 7. The bond strength of the reference case and all repair materials. (% above the bars represents the difference of bond strength of repair material compared with the reference case).

Table.2 summarizes viscosity measurements, shear stiffness defined as the slope of the linear part of the load-displacement curve, displacement at peak load, and toughness calculated as the area under load-displacement curve for all repair materials.

Table.2: viscosity, shear stiffness, displacement at peak load, and toughness for all repair materials.

Material	Microfine cement	Neat Epoxy	0.25% ANPs	0.5% ANPs	1.0% ANPs
Viscosity [cps]	250±52	204±8	209±8	216±10	221±8
Shear stiffness [kN/mm]	11.0±0.09	10.9±0.49	10.7±0.8	11.1±0.1	11.2±0.5
Displacement at peak load [mm]	0.75±0.01	4.84±0.20	4.09±0.13	3.54±0.06	3.39±0.04
Toughness [N.ma]	21.7±0.4	145.7±0.5	141.4±1.2	180.7±1.9	186.7±2.4

Fig. 8 shows the viscosity measurements for ANPs-epoxy nanocomposites compared with microfine cement. It was found that all ANPs-epoxy nanocomposites have viscosity lower than microfine cement. It was also found that incorporating ANPs in epoxy resin have a minor effect on epoxy viscosity. The maximum increase in viscosity of ANPs-epoxy polymer nanocomposite was found to be 8.2% compared with that of neat epoxy. The displacement at peak load for microfine cement and ANPs-epoxy nanocomposites is shown in Fig. 9. Although the results show that incorporating ANPs in the epoxy resin significantly reduces the displacement at peak load, the displacement at peak load of all ANPs-epoxy nanocomposites is significantly higher than microfine cement. Fig. 10. Shows The toughness of ANPs-epoxy nanocomposites compared to microfine cement.

Statistical analysis using student t-test with 95% level of confidence shows that the difference in viscosity of ANPs-epoxy nanocomposites was significantly different than that of microfine cement. Statistical analysis also shows that the difference of stiffness among all repair material was insignificant. It was also found that the difference in toughness between all ANPs-epoxy nanocomposites and microfine cement was statistically significant. However, there was no significant difference in toughness between neat epoxy and 0.25% ANPs-epoxy nanocomposite.

Fig. 8. Comparison of the viscosity between polymer nanocomposites incorporating 0% (Neat) 0.25%, 0.5%, and 1.0% ANPs and microfine cement. % represents the difference in viscosity of polymer nanocomposites compared to the microfine cement.

Fig. 9. Displacement at peak load of the microfine cement and all ANPs-epoxy nanocomposites. (% above the bars represents the difference of displacement at peak load of ANPs-epoxy nanocomposites compared with the microfine cement).

Fig. 10. Toughness for the microfine cement and all ANPs-epoxy nanocomposites. (% above the bars represents the difference of toughness of ANPs-epoxy nanocomposites compared with the microfine cement). Photomicrographs of the repaired shale interface with Type G cement using microfine cement, neat epoxy, and 1.0% ANPs-epoxy polymer nanocomposite are given in Fig. 11, Fig. 12 and Fig. 13 respectively. As shown in Fig. 11, using microfine cement as a repair material a gap at the shale-cement interface can be observed. It is important to note that such gap was not uniform and the width of the gap ranges from 3 μm up to 40 μm along the interface. These gaps might be formed due to shrinkage of microfine cement during its hydration. Such gaps between microfine cement and shale surface could explain the low bond strength in case of microfine cement compared with reference case.

Fig. 11. Microscopic images of shale-microfine cement interface with two different levels of magnification showing areas with gap between microfine cement and shale.

Photomicrographs of the shale-cement interface repaired with the neat epoxy and 1.0% ANPs-epoxy nanocomposite, shown in Fig. 12 and Fig. 13, respectively, show no gaps and demonstrate the ability of epoxy with and without ANPs to flow and seal the shale-cement interface. A close look at Fig. 12 and Fig. 13 shows the ability of the ANPs-epoxy nanocomposite to infiltrate into the porous shale interface and fill the microcracks at the shale surface. This ability of epoxy and ANPs-epoxy nanocomposite to penetrate the shale microcrack network at the interface enables creating mechanical interlocks in addition to the adhesion between epoxy and shale. These interfacial microcracks at the shale surface also provide potential leakage pathways and thus compromise wellbore seal integrity. The penetration of the epoxy nanocomposite repair material not only improves the shale-cement bond strength, but it also seals leakage pathways adjacent to the interface and thus improves wellbore seal integrity. The improved shale-cement bond strength when epoxy or epoxy-ANPs nanocomposites were used for repair can be attributed to the improved cement-shale interface microstructure.

Fig. 12. Microscopic images of shale-neat epoxy interface with two different levels of magnification showing the ability of the neat epoxy repair material to completely fill the gap at the shale-cement interface.

Fig. 13. Microscopic images of shale-1.0% ANPs-epoxy polymer nanocomposite interface with two different levels of magnification showing the ability of the epoxy repair material to completely fill the gap at the shale-cement interface.

FTIR spectra of neat epoxy and epoxy incorporating nano-alumina (0.5 and 1.0% ANPs) were obtained to compare chemical changes of the curing process of epoxy as shown in Fig. 14. The FTIR spectra show the traditional band of epoxy where absorption bands corresponding to C-H appear at $(2850\text{--}2930\text{ cm}^{-1})$, epoxide

ring ($\sim 825\text{ cm}^{-1}$), N-H band of primary amines ($1585\text{--}1610\text{ cm}^{-1}$), O-H groups ($\sim 3350\text{ cm}^{-1}$), C-N band ($1030\text{--}1115\text{ cm}^{-1}$) and ether bands ($\sim 1230\text{ cm}^{-1}$). The general illustrations of the chemical structures of the Novolac epoxy resin and its curing process can be found elsewhere (Golru et al. 2014). It can be clearly observed that addition of a small amount of ANPs (0.5 or 1.0%) to the epoxy resin caused a significant increase in the epoxy ring, O-H and primary N-H band intensity. This may be attributed to the effect of ANPs 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 (Brand et. al., 2004).

Fig.14: FTIR spectra of neat epoxy and epoxy incorporating 0.5 and 1.0 % ANPs showing the significant changes appearing in the spectra using ANPs compared to the neat epoxy.

It is interesting to note that both ANPs contents give the same effect on the curing process of epoxy. 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 a relatively small amount of ANPs about 0.50%. This can be understood from the higher peak 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 neat epoxy. This can be explained by the ability of ANPs to hinder epoxy curing due to steric hindrance effect of ANPs reported by Ramezanzadeh et. al. (2011). The steric hindrance effect results in decreasing the reactivity between the epoxy functional groups and polyamide

hardener. Such effect is attributed to the amphoteric nature of alumina nanoparticles which (Kardar et al., 2008, Sharifi Golru et al., 2014). The ability of ANPs to limit epoxy curing makes the unreacted epoxy groups available to react with other interfaces that epoxy is adhered to. This explains the ability of ANPs-epoxy nanocomposite to have much improved bond strength to both shale and cement compared with neat epoxy. A schematic of cured neat Novolac epoxy and Novolac epoxy incorporating ANPs based on the above FTIR analysis is shown in Fig. 15.

Fig. 15: A schematic showing the chemical structure of cured novolac epoxy (A) neat Novolac (B) Novolac epoxy incorporating ANPs.

The above FTIR observations explain the increase in the repaired shale-cement bond strength by 29% when ANPs were incorporated in the epoxy resin compared with neat epoxy. Furthermore, limiting epoxy curing using ANPs, enables creating a more flexible ANPs-epoxy compared with neat epoxy. The increase in epoxy-nanocomposite flexibility is represented by the higher toughness (energy absorption) of ANPs-epoxy nanocomposites compared with neat epoxy. The flexibility of the ANPs-epoxy nanocomposite can be explained by a reduced epoxy cross-linking.

To confirm the significance of ANPs on epoxy cross-linking, DMA testing was conducted on neat epoxy and epoxy incorporating 0.25%, 0.5%, and 1.0% ANPs. The suggested degree of crosslinking measure (X-Link) was calculated using Equations (2), (3) and (4). Fig. 16 shows the degree of crosslinking for neat epoxy, 0.25% ANPs-epoxy nanocomposites, 0.5%-ANPs epoxy nanocomposite and 1.0% ANPs-epoxy nanocomposite. The results show that incorporating 0.25% ANPs in the epoxy resin reduces the cross linking by only 4.9% which can explain the insignificant change in bond strength between ANPs-epoxy nanocomposites incorporating 0% (Neat) and 0.25% ANPs. On the other side, incorporating 0.5% and 1.0% ANPs reduces epoxy crosslinking by 15.8% and 16.4% respectively. The above analysis confirms the FTIR observations and is consistent with the observation that incorporating ANPs results in a more flexible epoxy nanocomposite compared with neat epoxy. A relatively flexible repair material with good bond strength to both shale and cement surface shall provide more stable long-term repair solution for its ability to deform in response to changes in wellbore conditions (stress, temperature, humidity) without cracking. Finally, DMA observations confirm that 0.5% ANPs per weight of the epoxy resin might be the optimal content in producing Novolac epoxy nanocomposite for repair for its limited significance on viscosity and low cost compared with higher ANPs contents. The choice of 0.5% ANPs can be justified by the insignificant improvements observed using 1.0% ANPs as confirmed by bond strength testing, FTIR and DMA observations. The use of 0.5% ANPs still provides the necessary strength and flexibility for the repair material.

Fig. 16. X_{link} : A measure of the degree of crosslinking for neat epoxy, 0.25% ANPs-epoxy nanocomposite, 0.5% ANPs-epoxy nanocomposite, and 1.0% ANPs-epoxy nanocomposite.

It is important to note that all the experimental investigations presented here were conducted on a smooth shale surface. Shale roughness, temperature and environmental condition (e.g. presence of carbonates) shall be examined in future work. Future experimental program shall also investigate the effect of shale roughness and surface chemical exposure (existence of carbonated brine and effect of salinity) on the bond strength of epoxy nanocomposites. In addition, relatively small crack sizes (10-100 microns) will be examined to investigate the ability of epoxy nanocomposite and microfine cement to flow in much smaller microcracks compared to those reported here. Furthermore, time dependent rheological properties of epoxy nanocomposites including the effect of creep and cyclic loading (fatigue) on cement-shale interfacial bond strength shall also be investigated. Finally, field trials of the proposed polymer nanocomposites will be necessary to identify the optimal content of nanomaterials to achieve field performance needs.

5. Conclusions

Novolac epoxy incorporating aluminum nanoparticles is being considered as a repair material for restoring wellbore seal integrity. Novolac epoxy nanocomposite incorporating 0.5% ANPs by weight of the epoxy resin proved to be a good repair material for shale microannulus with improved bond strength and excellent flexibility. Viscosity tests show that all ANPs-epoxy nanocomposites have viscosities that are comparable to that of microfine cement which might enable using ANPs-epoxy nanocomposite as repair material for microannulus cracks. The epoxy-nanocomposite repair material has a bond strength that is an order of magnitude higher than the industry standard for microfine cement repair material. Push-out tests were conducted to examine the bond strength of different repair materials including microfine cement and Novolac epoxy nanocomposites incorporation 0% (Neat), 0.25%, 0.5%, and 1.0% aluminum nanoparticles. The push-out bond strengths were compared with a reference case where Type G cement was cast directly around the shale core. Microstructural investigations were conducted to understand the behavior at the interface using microscopic images, FTIR and DMA.

The experimental investigation showed that microfine cement is unable to completely fill the gap between shale and cement and thus has a bond strength that is 21% lower than the reference case. In contrast, ANPs-epoxy nanocomposites had a bond strength that is 250% higher than the reference case. Microscopic investigation of the shale-cement interface shows microfine cement was unable to completely fill the gap and microcracks along the interface with widths up to 40 μm remaining open. However, no gap was observed with ANPs-epoxy nanocomposites. Furthermore, the ANPs-epoxy nanocomposite was able to penetrate the shale porous surface and establishes an epoxy network inside the shale providing mechanical interlocks that further improves the interface seal by blocking those potential leakage pathways. Moreover, it was found the difference in stiffness of the microfine cement and all ANPs-epoxy nanocomposites was statistically insignificant. In addition, the displacement at peak load and the toughness of ANPs-epoxy nanocomposites were significantly higher than the displacement at peak load and toughness of microfine cement.

FTIR and DMA measurements of ANPs-epoxy nanocomposites showed that ANPs interfere in the epoxy polymerization process and limits the reaction between the resin and the hardener. This was confirmed through FTIR spectra and by estimating epoxy crosslinking using DMA testing. The limited epoxy reactivity in the presence of ANPs leaves the epoxy groups unreacted which improves the bond strength at the cement-shale interface. The limited cross-linking also provides a flexible epoxy that shall enable a good long-term seal with improved ability to respond to shock waves and variability in temperature and humidity.

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

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