

Extending the Service Life of Crude Oil Export Line using PIPEASSURE[™] Composite Overwrap Repair System

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¹ M.A Nurnisham (Field Engineer, Pipeline Division, Innovative Oilfield Services, Bangi, Malaysia) ^{*}nurnisham@iossb.com.my ABSTRACT

Corrosion failure of steel pipelines has become highly expensive maintenance in oil & gas industry. Many of the structures affected are those in marine environments, and some are even critical lines. Fibre reinforced composite wrapping is one of the most cost-effective solution for corrosion prevention in high humidity atmosphere. One such case is discussed here which consist of the installation of PIPEASSURE™, a novel epoxy-glass fibre composite wrapping to provide corrosion barrier and strengthening of a 30" carbon steel crude oil export line situated directly across a river. From the data collected during site assessment, the remaining strength of the pipeline was calculated to be less than 1 year using ASME B31.G manual. Subsequently, ISO TS 24817 was used as the basis for engineering design of the live repair for a design life of 5 years. After 3 days of curing, post installation inspection reveals no discontinuities on the repair when holiday test was conducted. Hardness test result was found to be satisfactory and comply with client's acceptance criteria. The successful rehabilitation of the pipeline using PIPEASSURE[™] helped the client avoid costly shut down if the pipeline is to be cut and replaced.

Keywords: PipeAssure, corrosion failure, live repair, composite wrapping, integrity

INTRODUCTION

Pipeline is the lifeline of oil & gas industry. Any pipeline or piping failure is definitely a nightmare for oil & gas operators. Such failure might cause massive losses to operating company in terms of people, environment, asset and also reputation. Hence, operator will be on constant alert to avoid facing a loss of containment incident. Maintenance cost for pipelines can be costly however as saying goes 'prevention is better than cure', the cost of failure will definitely dwarf that of maintenance(1). As such, operators must balance between tight maintenance budget with pipeline integrity and ultimately flow assurance.

There are multiple approaches for a successful pipeline repair whether it is leak repair, strengthening or simply corrosion protection. Total replacement via cut-and-replace provides permanent solution; however it requires costly shutdown and loss of production besides having to deal with hot-work. Mechanical steel split sleeve provides best structural reinforcement however its deployment can be very slow due to long lead time for fabrication and expensive installation cost especially in offshore. Among others, composite wrapping provides the best of almost every aspect due being cost effective and fast deployment. In most cases, live repair can be done without having to shut down the line under repair.

PIPEASSURE[™] COMPOSITE OVERWRAP REPAIR SYSTEM

PIPEASSURE[™] is a novel pre-impregnated composite resin system for pipeline repairs, both onshore and offshore. The system was jointly developed by PETRONAS Research SdnBhd (PRSB) from Malaysia and Commonwealth Scientific and Industrial Research Organisation (CSIRO) based in Melbourne. It consists of "E-Glass fibre" pre-impregnated with a proprietary underwater epoxy resin formulation. The glass fibre content enables cheaper repairssince glass fibre is cheaper than carbon fibre, despite losing out in terms of strength and stiffness of fibre(2). The resin is designed to be hydrophobic, which keeps moisture away from bare metal thus providing effective corrosion protection and pipe reinforcement properties. Controlled manufacturing process gives the system very homogenous fibre to matrix ratio as compared to wet lay-up system. This in turn provides superior mechanical interlocking and adhesion strength, both in lap shear and transverse direction.

Unlike other competing products, PIPEASSURE[™] is curable underwater and is capable of withstanding wet environments without loss of adhesion and mechanical properties. The system was designed to perform in accordance to two international standards; ISO TS 24817 and ASME PCC-2 making it suitable for almost all sorts of repair in the oil & gas industry.

Innovative Oilfield Services SdnBhd (IOSSB) signed a commercialisation agreement with PETRONAS Technology Ventures SdnBhd (PTVSB), the technology commercialisation arm of PETRONAS. IOSSB as the licensee was appointed the official applicator for PIPEASSURE[™]. Till date, IOSSB has successfully completed numerous pipeline and piping rehabilitation works in various oil & gas facilities, both onshore and offshore.

CASE STUDY: 30" CARBON STEEL CRUDE OIL EXPORT LINE REHABILITATION

One such case of PIPEASSURE[™] application is discussed in this paper. IOSSB was invited to provide corrosion barrier and strengthening maintenance work on 30" crude oil export line in Miri, East Malaysia. This particular line is very critical to our client's operation since crude oil will be exported from the terminal via this line during single buoy mooring (SBM) loading to tanker. During peak loading, the line transports up to 130,000 barrels of oil per day, making it also critical to client's coffer.

Defect Assessment

The pipeline is located in a swampy region alongside Miri coastal land, right behind the process area of the terminal. A section of the 2 km long pipeline is located directly across the Lutong River. This section will be partially submerged during high tide and at times exposed to impact from logs. Latest inspection report reveals severe external corrosion due to high humidity with multiple pittings and gorges. Some areas of the pipe possess serious integrity issues with wall loss up to 70% from the original wall thickness. This led to the service request by the client to avoid any catastrophic failure. Summary of the defect assessment is as per Table 1 below.

Table 1: Summary of Defect Assessment

Pipe Material	Pipe size (inch)	Nominal Wall Thickness (mm)	Minimum wall thickness (mm)	Maximum defect depth [mm]	Length of repair [m]
API 5L X52	30	12.7	4.0	8.7	4.0

Design Calculation

Based on the site assessment and inspection report, IOSSB recommended PIPEASSURE[™] as the solution for this repair due to its superior mechanical properties, cost effectiveness and fast deployment. The idea behind pipeline strengthening is to restore the integrity and pressure containment capacity of the pipe to that of its design.As a start, ASME B31G-2009was used to determine of remaining strength of the pipeline(3). Based on the rate of corrosion and corrosion allowance, the remaining life was found to be less than a year. The result was used as input for ISO TS 24817 to determine the minimum laminate thickness, tmin required for this particular repair as given by Eq. 1 below(4).

where

D	= external diameter [mm]
5	= remaining pressure capacity of pipe [MPa]
E	= circumferential modulus of PIPEASSURE [™] = 15400 [MPa]
E	= modulus of substrate[MPa]
P_{eq}	= equivalent internal pressure [MPa]
P _s	= maximum allowable operating pressure, MAWP [MPa]

As a minimum, the repair was engineered for a design life of 5 years since the pipeline is scheduled to be decommissioned and replaced in year 2016. The required number of layers can be easily calculated by dividing t_{min} with the ply thickness of PIPEASSURE^{**}, *t* which is roughly 0.8mm. Since the wrapping will be done spirally with 50% overlap, one

wrap is equivalent to two layers. The required wrap angle and length of the length of repairs and 4 readings at cardinal clock position at each each wrap, L_wi.e. length of PIPEASSURE[™] material required for one

complete wrap is calculated using Eq. 2 and Eq. 3 respectively(5).

$$tan\theta=(2\pi) (D/w)$$
(Eq.1)
 $L_w = \frac{L}{cos\theta} + 2\pi (D+4nt) \cos \theta$ (Eq.2)

where

$$\begin{aligned} \theta &= \text{wrap angle } [^{\circ}] \\ w &= \text{width of PIPEASSURE}^{\text{\tiny ms}} \text{ tape } = 300 \text{ [mm]} \\ L &= \text{length of repair [mm]} \end{aligned}$$

Summary of the design calculation is tabulated in Table 2 below.

Table 2: Summary of Design Calculation

Design pressure [bar]	Design temperature [°C]	Minimum laminate thickness [mm]	No of wraps	Length of wrap [m]	Wrap angle [°]	No of rolls
44.1	43	9.6	6	68.0	86.4	20

Installation Procedure

Since PIPEASSURE[™] is a pre-pregsystem; it can be applied much faster than wet lay-up system which requires time consuming field impregnation prior to application. The frozen roll of PIPEASSURE™ is left to thaw for few hours while preparation work was done. Once soft, the PIPEASSURE[™] tape must be prepared for wrapping by first cutting the tape to Lw and tapering the ends. The taper length is double the circumference of the pipe.

The system is designed best to work when applied to bare metal, thus the pipeline section to be wrapped was grit blasted up to SA 2.5. The surface was then cleaned using acetone as per SSPC-SP1 requirement to remove any impurities prior to application of metal recovery compound (MRC). The load transfer material was used to fill up any wall loss and make up the surface profileof the pipe. The fast acting MRC cured in approximately 5 minutes, after which rough surfaces weresmoothen out using sand papers. The prepared surface was then coated with base coat of primer. The PR25 primer comes in two components, epoxide base (Part A) and polyamine hardener (Part B). Both parts were mixed with ratio of 100:17 and mixed portion has a pot life of roughly 45 minutes. The primer was then applied on the bare metal surface of the pipe using roller brush.

To begin wrapping, the tapered end of the tape was aligned at the edge of repair zone perpendicular to the pipe's axial direction. A 50% overlap was maintained at all times as the material was spiralled upwards in clockwise direction. Iron roller was used to squeeze out any air bubbles in between layers. Whenever one roll of PIPEASSURE™ was exhausted during a wrap, another roll was used to continue the wrap using butt joint, by overlapping the tape by 2 inches. The first wrap terminates at the opposite edge of the repair zone. Subsequent wraps were applied by repeating the same steps with alternating wraps beginning at opposite edge of the repair zone.

Once all six wraps were completed, final coat of primer was applied thoroughly on top of the PIPEASSURE[™] wrappings especially along the edges of the wrap to avoid any water ingress. Finally, cling film was wrapped along the length of repair to avoid any contamination and to ensure proper curing.

Post Installation Inspection

After 3 days of curing, the site was revisited for post installation inspection, which covers general visual inspection, Holiday test and Shore D hardness test. The wrapping was visually inspected for any delamination or disbondment of layers after removing the cling wrap. Holiday testreveal no discontinuities and result was found to be satisfactory in accordance to NACE RP0188-99 requirements i.e. no void, leak or pinhole. Shore D hardness test was conducted to measure the degree of curing. The measurement was taken at 3 locations along

location. The acceptance criterion for the test is 70 Shore D units. Result as per Table 3 below.

Area	Right Edge	Middle	Left Edge
12 o'clock	74	75	78
3 o'clock	78	72	77
6 o'clock	70	68	71
9 o'clock	78	78	75

CONCLUSION

Overall, the successful rehabilitation of the pipeline has further increased the client's satisfaction and trust on PIPEASSURE[™] as composite wrapping of choice. The system may not be the right repair option every time but it is a viable solution for pipeline rehabilitation especially during live repairs when operators can't afford costly shutdown.PIPEASSURE[™] technical capabilities such as curable in wet condition and superior adhesion strength gives the system competitive advantage over other competitors in the market. Being a cost effective solution compared to other alternative repair method, PIPEASSURE™ has great prospect to convince operators especially those with tight maintenance budget.

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Composite Polymer Electrolytes Based on MG49 and Cellulose from Kenaf as Reinforcing Filler

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ABSTRACT

The aim of this project is to explore the possibility of using celluose from biomass such as kenaf in solid polymer electrolyte in order to increase the mechanical performances at the same time maintaining its ionic conductivity. Lithium-conducting composite polymer electrolytes based 49% poly (methyl methacrylate) grafted natural rubber (MG49) were prepared from cellulose which was extracted from kenaf fiber and lithium triflate salt by solution casting. Prior to that kenaf fibers undergo several treatments (alkali, bleaching) in order to yield the white cellulose. White cellulose then treat with silane to decrease hydrophilic nature of CF which was then used as reinforcing filler in the composites polymer electrolytes. High performance composite electrolytes based on cellulose were prepared with various composition of filler (0-10 wt%). Field emission scanning electron microscopy (FESEM) were used for morphology studies of kenaf fiber for each stage of treatments. The films were analyzed by electrochemical impedance spectroscopy (EIS). Ionic conductivity measurement showed that the addition of various wt% of cellulose give a weak decrease of conductivity with respect to unfilled polymer electrolytes. The effect of different cellulose content of composite polymer electrolytes on mechanical properties was evaluated through tensile modulus test. Result showed that the composite electrolytes with 4 wt% cellulose exhibited high mechanical performance.

Keywords: Composite Polymer Electrolytes, Kenaf, Cellulose, Ionic Conductivity, Mechanical Properties

INTRODUCTION

Natural fibers, as reinforcing elements in polymer composites, offer several advantages over conventional reinforcing materials such as glass fibers. Due to their low tool wear, low density, cheaper cost, availability, and biodegradability, cellulose serves as promising candidates for the preparation of biocomposites [1]. A potential characteristic of cellulose fiber (CF) in the composite fibers made CF has broad range applications such as filler in the preparation of polymer electrolyte composite. Solid polymer electrolyte (SPE) was used as ion-carriers in secondary batteries lithium polymer. SPE have grabbed attention many researchers because the potential of SPE as rechargeable batteries, fuel cells, light-emitting fuels, and many other applications in electrochemistry [2]. One of main advantages of SPE was free solvent which have possibility to reduce electrolytes thickness and result in decreases internal resistance of the battery at the same time maintaining conductivity [3]. The main objective in polymer research is to develop polymer systems with high ionic conductivity with the encouraging mechanical properties. The good interactions between CF/MG49 provide better final properties of composite polymer electrolyte.

Moreover, polymer electrolytes must be exhibit, in addition to high conductivity and wide electrochemical stability, high thermal and mechanical performances for safety and performances reasons. Since the original work of Weston and Steel (1982) that use α -Al₂O₂ as inorganic filler in polymer electrolytes, the understanding of impact of filler in the polymer electrolytes have been extensively studied. Recent year, research on the use of cellulosic resources as filler in the SPE has grown rapidly. In addition, these fibers showed better thermal properties that make it suitable to be used as filler in the composite polymer electrolytes [4].

Kenaf (*Hibiscus cannabinus*) is a plant that belongs to the Malvaceae family and grows commercially in many places worldwide. The fibers derived from the outer fibrous bark, which are also known as bast fibers, have cellulose contents ranging from 30% to 63%, making them a good source for cellulose extraction [5]. Furthermore, the use of kenaf or lignocelluloses fiber as organic filler is a wise step in replacing

inorganic filler because it is cheap, easily available, the resources are not limited to, improving the mechanical properties of composites and is not harmful to health.

The aim of this project is to explore the possibility of using cellulose from kenaf in modified natural rubber (NR) based SPE in order to improve the mechanical performances at the same time maintaining its ionic conductivity. Extractions of cellulose from kenaf undergo several treatments which are alkali and bleaching treatment. Treatment CF with silane decrease its hydrophilic to make sure it compatible with matrix which is MG49 that more hydrophobic [1]. So it can interact well in matrix in preparation SPE. Morphology analysis was evaluated to see the effect of different stages of kenaf fiber treatment. The effects of different filler contain on mechanical performances and conductivity was investigated.

EXPERIMENTAL

Materials

Kenaf fiber was provided by Kenaf Fiber Industry Sdn. Bhd. (Malaysia). Sulphuric acid (98%), sodium hydroxide (99%), sodium chlorite (80%) and acetic acid glacial (99.5%) were purchased from SYSTERM-chemAR (Malaysia) and Sigma-Aldrich (Germany). All the chemicals were used without purification. MG49 was commercially obtained. Lithium triflate (LiCF₃SO₃) salt were supplied by Fluka.

Preparation of cellulose from kenaf

Preparation of white cellulose consisting two steps, the first step was alkali treatment and followed by bleaching process according to Kargarzadeh et al. [5]. Prior to that, kenaf fibers were cut into small pieces. Briefly, kenaf fiber was treated with 4%wt NaOH solution in round bottom flask under mechanical stirring at 80°C 3 h. Reflux process was conducted three times and it was then filtered several times using distilled water to remove alkali component. 5% (w/v) of fiber was undergoing bleaching treatment 4 times with 1.7% (w/v) of sodium chlorite solution and acetic buffer at 80°C under mechanical stirring for 4 hours. The extracted cellulose and was allowed to cool and then filtered using excess distilled water and air dried [5]. Finally, the cellulose was soaked in 5% concentration of silane for 1 h, filtered using distilled water and then dried at room temperature.

SPE Film processing

All polymer electrolytes samples were prepared by the solution casting method [2, 6]. MG49 rubber was sliced into grain size and then was dissolved in conical flasks containing THF. After 24 h, the solution was stirred with magnetic stirring for the next 24 h until complete dissolution of MG49 into clear viscous solution. 20 % wt LiCF₃SO₃ salt was stirred in THF solution for 12 h and it was added to the MG49 solutions for the next 24 h with continuous stirring. White cellulose was dissolved in THF after undergoes solvent exchange (cellulose suspension, acetone, THF). THF suspension of cellulose was added to the MG49/salt in conical flask with continuous stirring for 24 h to obtain a homogeneous solution. The electrolyte solutions were cast onto a glass petry dish and the solvent was allowed to slowly evaporate in a fume hood at room temperature. Resulting films were dried under vacuum oven for 24 h at 50°C to remove remaining solvents. The samples were then stored in desiccators for further use [6].

Characterization

The morphology of the fibers after each treatment was investigated using a Zeiss Supra 55VP field emission scanning electron microscope (FESEM) with a magnification of $400\times$. All samples were sputter-coated with gold before observation to prevent charging.

The ionic conductivity measurements were carried out by EIS using a high frequency resonance analyzer (HFRA) model 1255 with applied frequencies from 1MHz to 0.1 Hz at a perturbation voltage of 1000mV. All experiments were conducted at room temperature [1]. The ionic conductivity [σ] was calculated according to the equation

 $\sigma = [l/(A.Rb)]$ (Eq.1)[6]

The bulk resistance [Rb] was obtained from the intercept on the real

impedance axis (Z-axis), the film thickness [l] and the contact area of the thin film $[A = \pi r^2 = \pi (0.80 \text{ cm}^2)^2 = 2.01 \text{ cm}^2]$.

Mechanical performance of the films was evaluated with universal testing machine (Instron model 5566, USA) at room temperature according to ASTM D882. A crosshead speed of 50 mm/min, initial grip distance of 40 mm and load cell of 50 N were used to perform this test. The samples were cut into a dumbbell shape and average value of 7 replicates for each sample was taken.

RESULT AND DISCUSSION Morphology Studies

Figure 1 presents field emission scanning electron microscope (FESEM) of kenaf fiber after different stages of treatment. Raw fiber (Figure 1a) had a rough surface with impurities and contains by cellulose, hemicellulose, pectin, lignin, and other chemical composition. However, after alkali treatment (Figure 1b) the surface become less rough. The important modification that was done by alkaline treatment was the disruption of hydrogen bonding in the network structure. From the observation, almost all impurities have been removed from the fiber surface which induced the separation of fiber bundles into individual fibers [5]. This treatment removes certain hemicelluloses, lignin, wax and oils covering the external surface of the fiber cell wall, depolymerizes cellulose, and exposes the short length crystallites [2,8,1]. As for kenaf fibers after bleaching, more significant physical change on the fibril surface can be observed (Figure 1c). Fiber has decomposed to the individual microfibril which is caused by the removal of most of the remaining lignin fiber. In other words, this treatment reduces fiber diameter and thereby increases aspect ratio[1].



Figure 1: Micrograph FESEM for kenaf fiber a) Raw b) Alkali treatment c) Bleaching

Ionic Conductivity

As can be seen from Table 1, the introduction of cellulose only had a modest influence on the ionic conductivity of the composite. The conductivity of the composite was reduced from $1.2 \ge 10^{-7}$ to $5.4 \ge 10^{-7}$ 10⁻⁸ upon introduction of 2% wt of cellulose fiber. However, the values of ionic conductivity in the composites remain higher with respect to unfilled SPE. A decrease of the ionic conductivity with the addition of tunicin whiskers in PEO based electrolytes was also observed by Azizi et al. [3]. The different in conductivity observed between filled and unfilled composite may be due to the existence of interactions between cellulose and MG49 or lithium salt [7]. Nevertheless, interactions between anions and surface hydroxyl groups of CF via hydrogen bonding lead to decrease the mobility of former [3]. The highest conductivity for filled polymer electrolytes obtained with 2 % wt of CF which is 5.4 x 10⁻⁸ Scm⁻ ¹compared others. This may due to the increasing of CF content result in increasing crystallization kinetic presence of CF, which undergoes crystallization process and reduce the mobility of lithium ion.

Cellulose content, wt%	Conductivity , o [Scm1]
0	1.2 x10 ⁻⁷
2	5.4 x 10 ⁻⁸
4	4.8 x10 ⁻⁸
6	1.4 x 10 ⁻⁸
8	7.5 x 10 ⁻⁹
10	9.6 x 10 ⁻⁹

Mechanical Properties

Tensile strength of SPE was determined and the results are plotted in Figure 2. As shown in Figure 2a, the tensile strength increased with cellulose loading with the optimum fiber loading at 4% due to effective interaction between CF/MG49/salt. This is explained by the increase of uniformity that contributes to the increase in strength, due to the removal of the impurities. The formation of a rigid percolating cellulose fiber network also assumed to be formed through strong hydrogen bonds interactions in cellulose fiber [3]. It is reported that alkaline resulting in better mechanical interlocking, and then increases the amount of cellulose exposed on the fiber surface. Thus the number of possible reaction sites was increase and has effect on the mechanical behavior of natural fibers [1]. From Figure 2b, the Young's Modulus also highest in 4 % cellulose loading and the value (995 MPa) was much higher than unfilled SPE (380 MPa). Generally, optimum tensile properties and Young's modulus are dictated by the volume of reinforcing fiber used for the composites [10]. However, when the percentage of CF further increased up to 6-10% the SPE tensile strength and Young's Modulus tends to stabilize. Rigidity of this network depends on the concentration of filler with respect to the interaction of filler/filler through the hydrogen bonding [9]. Addition of salt was induces the CF flocculation demonstrating the main role of the electrostatic interaction between cellulose and result in a loss homogeneity of the cellulose dispersion. Non uniform distribution of cellulose in the matrix, induces agglomeration hence restrict filler reinforcement within a polymeric matrix [9]. Therefore, the mechanical behavior of SPE will decrease for 6-10% wt of CF.



Figure 2: a) Tensile Strength b) Young's Modulus for SPE

Conclusion

Composite polymer electrolytes have been prepared using MG49, LICF3SO3 and cellulose from kenaf fiber. Alkali and bleaching treatment of kenaf fiber showed significant physical changes to the fiber. The effect of cellulose loading was investigated by EIS and mechanical test. The presence of cellulose fiber induces weak decrease of polymer electrolytes conductivity due to the interaction between cellulose and MG49 or salt. Cellulose fiber as reinforcing filler for SPE leads to improve the mechanical strength for SPE prepared even small percentage of CF was added.

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