

Enhance the Corrosion Resistance of Underground Petroleum Tanks with the Use of Fiberglass-Reinforced Composite

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ABSTRACT: *In the present study, attempts are made to enhance the corrosion resistance in underground storage tanks. For this purpose glass fiber reinforced unsaturated polyester was used to coat the underground storage tank. The coating was applied by the hand layup technique. Multiple layers of glass fiber reinforced coating were applied, with the matrix composition of 97% polyester, 2% hardener, and 1% cobalt as an accelerator. Better corrosion resistance was observed when tested for the corrosion activity of the reinforcing steel with applied coating. It also provides better mechanical properties. For impact energy, the Izod test was performed. The mechanical properties and corrosion resistance were increased as increasing the fiber layers in the composite. This research is very helpful for future use as it provides a more cost-effective and better mechanical properties solution for the coating of the underground storage tank.*

KEYWORDS: *Glass-fiber reinforced composite; Unsaturated polyester; Petroleum tank; Corrosion resistance; Impact energy; Shear test.*

INTRODUCTION

Metal components outside petroleum fuel underground storage tanks (USTs) are prone to suffer from moderate to severe corrosion. Corrosion begins as pitting on the metal surface by deposition and creating holes in the UST systems where metal components are exposed. Pits may form as the penetration grows deeper. Over time, even a little corrosion pit might result in large emissions and it might lead to UST system failures and groundwater

contamination. Composites are designed materials made up of two or more components that have substantially distinct physical, chemical, and mechanical properties [1, 2].

These materials have noticeable advantages over other types of materials (metals, alloys, ceramics, and polymers) in that they can be produced with pre-set physical such as mechanical characteristics, chemical resistance, and thermal capabilities. These materials should be corrosion

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resistant, able to tolerate high temperatures, and easy to manufacture. Composite materials have been and will continue to be, employed to fulfill the demands of such sectors. The two main constituents of composite materials are matrix and reinforcements such as fibers. Because of its mechanical characteristics, cheap cost, and corrosion resistance, glass fiber is the most suitable reinforcement. The function of the matrix is to bind the fibers together and transfer the load to the fibers. It provides durability and structural stability. The function of reinforcements is to carry the load and provide toughness and resistance [3, 4].

Composites are classified based on matrix material, Metal Matrix Composite (MMC), Ceramics Matrix Composites (CMC), and Polymer Matrix Composites (PMC). Composites are also classified based on reinforcing material, particulate composites, fibrous composites, and laminate composites. There are two techniques for the fabrication of composites, open molding, and closed molding. A hardener is used as a part in certain types of mixtures for curing the matrix region; it can be used in the reaction (reactant) or used as a catalyst. The full potential of resin as far as its properties are concerned can only be achieved by the incorporation of the appropriate extent of the hardener. The hardeners commonly used in the composite industry are; amines, acid anhydrides, acids, phenols, alcohols, and organic peroxides. Moreover, metallic accelerators such as cobalt are used to enhance the ability of the hardener and make the resin cure as quickly as possible [5, 6].

Conventional mild steel tanks are used for underground petroleum storage but they are prone to corrosion. To avoid corrosion on the tank, anti-corrosion coatings are required annually for maintenance and mild steel tanks have to be replaced every 5-10 years. Applying the anticorrosion coatings or replacing tanks every 5-10 years requires an extended workforce with time-money consumption in the process. This study focuses on enhancing the corrosion resistance of underground petroleum tanks with the use of fiberglass-reinforced composite. This coating will prolong the life of mild steel tanks. Fiber-reinforced unsaturated polyester resin is used for coating the outer surface of underground petroleum tanks. The improved mechanical and chemical properties of fiber-coated mild steel tanks can reduce the maintenance cost and increase the life cycle of the tank. The coating is applied on mild steel plates in this study

by hand lay-up process in the laboratory. This study provides a low approach for improving corrosion resistance in underground storage tanks. The study's approach not only improves corrosion resistance, but also no such fillers, binders, or flame retardants added. This not only improves the mechanical properties of underground storage tanks but also enhances their chemical stability as well [7, 8]. Corrosion, or the deterioration of material caused by chemical or electrochemical interactions between material and its environment, has been a major concern in the industry for many years. There is no exception in the petrochemical industry, where corrosiveness is recognized as the leading cause of costly equipment breakdowns. Corrosion is a prevalent issue when fuel products come into contact with metals and alloys, whether they are produced, distributed, processed, or stored. Carbon-steel storage tanks built for long-term (at least five-year) oil storage may have an impact on the chemical strength of the oil (increased content of oxidation products) [9, 10]. Physical inspection revealed that the ratio of non-corroding parts of the steel plate to places where corrosion could occur was 300: 1. Tensile strength varied by less than 1%, suggesting that the steel did not lose strength or stiffness when immersed in an ethanol-gasoline blend. There was less than a 1% variation in tensile strength, showing that the steel did not lose strength or stiffness when immersed in an ethanol-gasoline blend [11, 12].

This research provides an overview of the evolution and standardization of exterior corrosion systems used under storage tanks for volatile and flammable liquids. This study begins by explaining the various types of corrosion prevention used in flammable and combustible liquid subsurface storage tanks. It then goes over the benefits and drawbacks of each rust prevention strategy. Underground steel storage tanks have evolved from unprotected steel to current covering technologies that give great corrosion protection while being environmentally benign during the last 50 years. Bitumen, plastic baggies, tape covers, coal tar epoxy, and 100 percent solid polyurethane coatings were among the corrosion-resistant materials employed. A large number of storage tanks and piping failures are associated with external corrosion, usually as a result of their exposure to corrosive soils, while only a tiny fraction contributes to internal corrosion. The tank materials do not corrode the polymeric material

or when a steel tank is outfitted with a thick coating of non-corrosive material. Fiberglass reinforced tanks produced with resins such as vinyl ester or epoxy are commonly utilized, although the tank's warranty is restricted to 65.5 degrees Celsius [13, 14].

Corrosion is more likely to occur in stainless steel under harsh environmental circumstances such as low pH, moderate temperature, and high chloride content. The scope of this research is to use the underground tanks for filling stations in urban lands where the land is considered to be moderately saline and precisely 5000 ppm of salt concentration is quite accurate for to be used for experimentation. Because of its mechanical characteristics, cheap cost, and corrosion resistance, glass fiber is the principal reinforcement utilized in polymeric corrosion-resistant constructions. Glass containers are utilized to handle corrosive chemicals since the medium has little or no impact on the container. Fiberglass products exclusively use thermosetting resin systems, of which there are two types: epoxy resins and polyester resins. Fiberglass reinforced tanks made with resins such as epoxy were frequently utilized, however, the tank's guarantee is limited to just 65.5 degrees Celsius [15, 16]. The lining system for fiber-reinforced plastic tanks can be fitted by hand or by spray. However, hand layup is the favored approach, even though it is significantly slower and takes more effort, as well as having a longer resin gel time than spray layup. However, hand layup provides a more uniform and consistent coating. Fiberglass reinforced linings are a low-cost approach for petroleum storage tanks. Because fiberglass reinforced plastic is a polymeric resin substance that is chemically resistant to corrosion and permeation to those pitting the metal surfaces. Steel tanks constructed and installed nowadays require additional containment to guard against corrosion and leaks with the help of exterior GRP coating. Fiberglass reinforced linings are a low-cost approach for petroleum storage tanks [17, 18].

EXPERIMENTAL SECTION

Mild steel

Mild Steel is low carbon steel, due to its excellent properties it has become in-demand material for various industries. Low-carbon steels have a carbon content ranging from 0.05 to 0.25 percent. Because of its low carbon concentration, this metal is extremely efficient.

It can be cut, machined, and constructed into complicated forms without causing equal pressure to be applied to the work. It also contributes to improved weldability and withstands changing loads [19].

Glass fiber

The following are some of the properties that have made E-glass so popular in fiberglass and other glass fiber reinforced composites: reasonably priced, high rates of production, extreme toughness, extensive stiffness, relatively low densities, non-flammable materials, heat-resisting, and excellent chemical resistance. E-glass fiber with a density of approximately 2.6 g/cm³ and tensile strength of about 3,000 MPa is used [20].

Unsaturated polyester resin

Unsaturated polyesters offer simplicity of dealing with, minimal expense, and dimensional stability just as great mechanical, chemical resistant, and electrical properties. Unsaturated polyester resins are the most affordable of the resin alternatives, giving the most efficient approach to incorporating resin, filler, and reinforcement. They are the essential resin matrix utilized in SMC (Sheet Molding Compounds) and MMC (Mass Molding Compounds) [21].

Procedure

The procedure is commenced when corrosion is buffed out of the Mild Steel (MS) plate. The plate is then cut into a length of 102mm, a width of 64.30mm, and a thickness of 4mm. Silicon carbide sandpaper with coarse grit is used to roughen the surface of the MS plate and allows the resin to firmly adhere to it. The coating of fiber-reinforced polyester is done by utilizing a hand lay-up process. Fig. 1 shows the sample formed using the hand lay-up technique. The hardener utilized with the polyester resin is named Methyl Ethyl Ketone Peroxide (MEKP). The variability in the proportion for a catalyst to resin is 2 percent hardener to the absolute volume of resin to be utilized. The curing time for the resin can be enhanced or reduced according to the amount of catalyst agent used in the process. However, it was observed adding under 1% or over 2% will affect the resin to cure incorrectly failing.

Liquid Cobalt Octoate, as a promoter is utilized in the curing process of unsaturated polyester resins when used in conjunction with catalysts. The reason for cobalt-based promoters is to accelerate the curing reaction of polyester



Fig. 1: Hand lay-up technique sample preparation

resins and permit them to cure at room temperature. The specific measure of promoter added to the resin will rely upon the resin utilized. Generally, 1% of cobalt is added (depending upon the weightage of resin). Promoters should never be mixed directly with a catalyst as they result in a flammable reaction. This is why it is necessary to guarantee all promoters are blended in with the resin before adding the catalyst. Completely blended resin is applied to the MS plate by brushing and using a paint roller. Fiberglass reinforcement is physically positioned randomly on the resin. Paint rollers are utilized to consolidate the resin, completely wetting the reinforcement and eliminating the entrapped air in between. On the fiberglass mat, another layer of resin is applied by brushing and utilizing a paint roller. The following layers of fiberglass reinforcement and resin are applied and consolidated by paint roller until multiple layers of glass fiber are applied. The layers of the fiberglass are oriented randomly to provide isotropic macroscopic strength. The more planning time between the layers, the stronger the finished product will be. After the required layers are applied, the sample is put down for curing. After 6 hours the sample was fully cured and ready for testing. The tests carried out for the study are; the tensile test, Izod impact test, corrosion test, and single-lap shear test for adhesion.

Tensile testing

Tensile testing according to ASTM D3039 is used to determine the force necessary to break a polymer composite specimen as well as the amount to which the specimen stretches or elongates to that breaking point. ASTM D3039 specimen is a constant rectangular cross-section that is 25 mm (~1 inch) broad and 250 mm (~10 inches) long. To prevent grip slippage, adhesive tapes can be bonded

to the ends of the specimen. The specimen was tested in three different conditions, some were kept in an atmospheric environment and others are kept in soil with and without 5% of saline water content for at least 10 weeks of duration. Then tensile strength of each of them was performed to check if their tensile strength is affected under a specific environment. Tensile testing provides a stress-strain diagram that is used to calculate the tensile modulus with the ratio of material tensile stress along its deformation in terms of strain when undergoing elastic deformation before yield stress. The data is frequently used to specify a material, design parts to withstand application force, and as a material quality control check. Specimens are put in the grips of a Universal Test Machine (UTM) at a predetermined grip separation of 100 mm and pulled until failure occurs. The test speed for ASTM D3039 can be calculated by the material specification or the time to failure (1 to 10 minutes). For standard test specimens, a common test speed is 2 mm/min (0.05 in/min). With the help of an extensometer or strain gauge, elongation and tensile modulus are calculated.

Lap shear test

A peel test is carried out to test the adhesive nature of the composite bonded to the external surface. Both substrates can be either flexible or stiff. This adhesive nature, often known as a material's "stickiness," is a measure of the samples' resistance to separation from one another. This measured value may now be used to assess if the adhesive bond is strong enough for the application or whether an alternative adhesive or bonding method is required. The test specimen is held in place by a permanent grip with a grip separation of 140 mm in length. De-bonding or the separation of the two components is tested physically by applying axial tensile force. The maximum force observed during the test before the detachment of the coated surface from the metal surface gives the value of bonding strength in N. The top component is gripped in the moving vice, which is connected to a moving crosshead. The test speeds are typically set at 300mm/min.

Electrochemical measurements

Underground tanks are exposed to soil and minerals, and variance in temperature and other conditions on the ground is directly proportional to the exposed part of the tank. This results drastically in forming anodic and cathodic patches

on metal and resulting in electrochemical corrosion. The corrosion rate is deduced by doing electrolysis and following the procedure prescribed in ASTM C876 standard method in which half-cell potentials of mild steel plate reinforced with fiberglass composite are immersed in a solution of water and 5% wt of NaCl. The following parameters are noted before following the procedure prescribed above, such as; area (cm^2), time (h), density (g/cm^3), and initial weight (g). A rectangular cross-section bar that is 25 mm (~2 inches) broad, 250 mm (~10 inches) long, and 5mm (~0.2 inches) thick is used, large enough for appreciable changes to be observed. As mentioned in ASTM G31, those alloy constituent that tends to corrode substantially does not requires tedious tests to get definite corrosion rates. A comparative analysis with enough exposure time is good to find the characteristic difference with and without the coated sample. The testing method measures the loss mass, which can be used to calculate the corrosion rate due to general corrosion and not because of localized corrosion and hence can be determined by following Eq. (1) mentioned in ASTM G31 linked with ASTM G1. In this equation W_i is the initial weight, W_f is the final weight in grams (g), A is an area exposed in square centimeters (cm^2) t is the time of exposure in hours and ρ is the density in grams per cubic centimeter (g/cm^3) measured.

$$CR \left(\frac{\mu\text{m}}{\text{year}} \right) = \frac{8.76 \times 10^7 (W_i - W_f)(g)}{A(\text{cm}^2) \cdot t(h) \cdot \rho(\text{g} \cdot \text{cm}^{-3})} \quad (1)$$

Impact test

Izod impact testing is a technique for determining the fracture properties of polymer composites in impact tests. In this test, a pendulum will strike the specimen, and the potential energy following the parameter of the pendulum will be calculated based on the mass and drop height. Specimens with a different number of layers are tested to consider the moderate number of layers of glass fibers required for the composite. The Izod test consists of hitting an appropriate test item with a striker attached to the end of a pendulum. The test piece is secured vertically, with the notch pointing toward the striker. At the bottom of its swing, the striker strikes the test piece. A typical specimen for ASTM D256 measures 64 x 12.7 x 3.2 mm (2.5 x 0.5 x 1/8 in.). The typical specimen thickness is 3.2 mm (0.125 inches), although the breadth ranges from 3.0 to 12.7 mm (0.118 and 0.500 in). Although the impact

strength is directly calculated from the absorption of energy by the specimen by the instrument but Eq. (2) mentioned in ASTM D256 can also be used. In the corresponding equation, E_s is the impact energy absorbed by the sample when struck with the pendulum, h_m is the height of the pendulum at the released position, h_s is the height of the pendulum at the rebound position after the sample is struck, W_p is the weight of the pendulum striker, g is the acceleration due to gravity, b is the width (mm) and d is the depth of the specimen (mm) facing the striker direction measured.

$$E_s \left(\frac{\text{kJ}}{\text{m}^2} \right) = \frac{(h_m - h_s)(m) \cdot W_p(\text{kg}) \cdot g(\text{m} \cdot \text{s}^{-2})}{b(\text{mm}) \cdot d(\text{mm})} \quad (2)$$

Flexural strength

ASTM D7264 specifies how to test the flexural properties of GFRP using a rectangular cross-section bar supported on a beam and diverted at a steady rate on a three-point loading system. Since the underground tanks are spherical, circumferential stresses will be acting on the tank. This test will help to determine the strength of the material when subjected to three-point bending. A three-point loading system for center loading is described in the procedure. Typically, the specimen is placed on a support pin, and the loading nose is focused at the center with force, causing three-point bending at a predetermined rate. Flexural strength is calculated using Eq. (3) for three-point bending provided in ASTM D7264. In the following equation σ is the stress (MPa), F is the load applied in Newton (N), L is the length (mm), b is the width (mm) and d is the thickness of the specimen (mm) measured. The width of a standard specimen is 13 mm, the thickness is 4 mm, and the length is 20% longer than the support span.

$$\sigma(\text{MPa}) = \frac{3F(\text{N}) \cdot L(\text{mm})}{2b(\text{mm}) \cdot d^2(\text{mm}^2)} \quad (3)$$

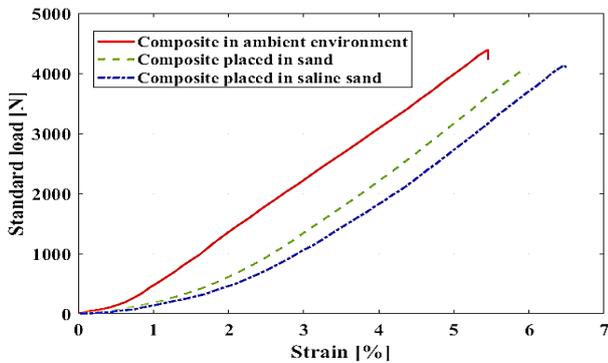
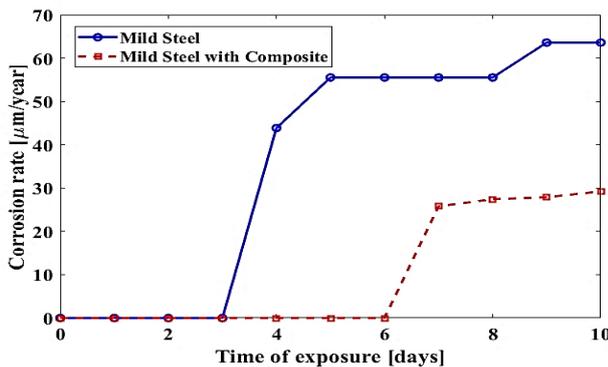
RESULTS AND DISCUSSION

Tensile test

Tensile testing is done on the composite to check whether the mechanical properties are changed or if it remains the same. Three different types of samples are tested; simple composite in an ambient environment, composite kept inside the soil, and composite inside soil with saline water. Composite with soil and saline water is given in this environment for 10 weeks and is then tested to compare

Table 1: Mechanical characteristics of the GFRP composite in different environmental conditions

Sample	Young's Modulus (MPa)	Tensile Strength (N/mm ²)	Elongation at break (%)
Composite in an ambient environment	125.58	58.9359	6.46736
Composite placed in sand	167.941	60.0403	5.64169
Composite placed in saline sand	269.838	60.9062	5.34343

**Fig. 2: Effect of tensile test on GFRP with different ground conditions****Fig. 3: Effect of corrosion rate with and without composite coating**

the results of simple composite. Tensile test results of individual samples are plotted concerning their corresponding environment that has been given.

Composite exposed under different environmental conditions are examined. As Fig. 2 suggests that maximum force required amongst three samples is for composite exposed to a sand and salt environment with the lowest elongation amongst the other two, in real conditions sand and salt are the most important aspects that need to be brought under consideration. In underground tanks, the maximum damage caused to steel tanks is due to the presence of minerals. Electrochemical corrosion causing in maximum damage to the tank externally and further results in the variance of its mechanical properties. However, comparing the other two results from Fig. 2,

it can be deduced that under harsh conditions such as the presence of salt in the soil, the composite shows a 1% decrease in its elongation under such conditions. However, the other two sample shows almost the same results with GFRP showing a decrease of 0.6% elongation. Table 1 concludes that the ultimate tensile strength shows very little variance when kept in different environment conditions although the elongation at break tends to decrease due to the effect of salt on the composite. Whereas Young's modulus is increased due to the stiffness of the composite with a change in pH of the environment resisting the elastic stretch in the composite [21, 22]. Hence, very less reduction is observed in elongation and tensile strength of material exposed to different environmental conditions.

Corrosion rate

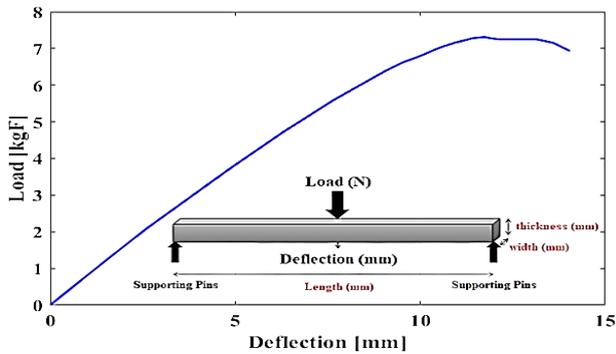
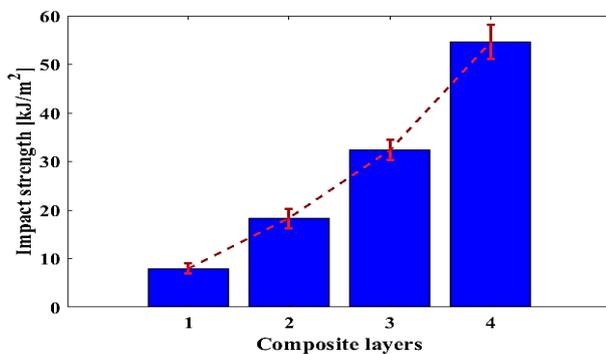
Two samples are prepared for the apparatus set up accordingly ASTM C876. One is for the metal plate without any protection or layer while the other is for composite. The measurement and the calculation part are explained in electrochemical measurement. The corrosion rate is calculated from the initial day of exposure. Fig. 3 shows the trend of both samples calculated through ASTM G31. Metal with no layer is what we see today in different applications. The trend in Fig. 3 signals an alarming situation as the rate of corrosion is well initiated from day 3. Conditions of soil vary according to the area. The experiment is done with 5% NaCl by weight. The region with more pH value will result in the occurrence of more corrosion. Meanwhile, in Fig. 3, GFRP on metal shows corrosion rate on a very small scale as compared to the metal plate. Since metal is directly in contact with soil and this case saline water. Whereas, GFRP on metal not only serves as a protective layer against corrosion but also helps to maintain the mechanical and chemical properties that can be degraded under such conditions [17, 18].

Flexural strength

Flexural strength shows the maximum compressive and tensile stress at the specimen's surface before failure

Table 2: Bonding characteristics of the GFRP composite with surface-treated metal

Sample	Tensile Modulus (MPa)	Ultimate Strength before detachment (N/mm ²)	Elongation before detachment(%)
Polished surface	150.325	26.0869	6.2859
Sandblasted surface	79.655	47.8260	8.8358

**Fig. 4: Flexural strength of GFRP composite****Fig. 5: Impact strength of GFRP with different layers of glass fiber embedded**

in bending as shown in Fig. 4. When subjected to three-point-to-point loads, the GFRP composite alone demonstrates axial load (force) at the rupture point was approximately 7.2 kg_F (~71N) with deflection up to 11 mm signifying structural toughness before it tends to fail. The flexural strength, using equation (3) is calculated to be 52.7 MPa with the dimensions specified in the previous corresponding section, demonstrating that bending stress is sufficient for the tank to resist circumferential stresses [16, 21].

Izod test

A composite sample of 2, 3, and 4 layers of glass fiber was made and their impact energy was tested. The results obtained are shown in Fig. 5. If the number of layers is insufficient, it will not assist to perform the function for which it was designed. If the number of layers of glass fiber

is increased, cracks between the layers of GFRP may form and eventually dissolve. Fig. 5 shows the moderate impact energy for three-layered GFRP which is the required toughness for underground tanks and crack prevention between the layers. Increasing the layer will increase the impact energy at the cost of the coated material [12, 13].

Lap shear test

Molecules binding together unlike materials are the adhesive property of a material. Mild Steel with two different surfaces is tested. One surface is smooth and polished while, the other one is rough, irregular, and sandblasted. Fig. 6 below shows the results of both samples when GFRP is made on the surface of each metal plate. Results are quite explanatory themselves, it was nearly impossible for the GFRP to show positive adhesive properties on polished surfaces. As there will be no interfacial bond making on the polished surface. Since the metal and GFRP show a very less adhesive nature, there is a possibility for the GFRP to be peeled off from the metal surface easily. However, irregular and rough surfaces prove to be more useful to enhance the adhesive property. Irregularities and pores provide the resin to adjust and bond itself with the metal surface providing an interfacial area to bind the composite and metal together. Fig. 6 shows a very large difference between force and % elongation of either sample before peeling off the surface. The sandblasted surface shows 50% more elongation than the polished surface. Whereas, the same results are observed in force required before rupture. An irregular surface requires 1700N more force before rupturing than a polished surface. The mechanism of adhesion in the presence of pores and roughness enhanced bonding between GFRP and mild steel plate as shown in Fig. 7 (a, b). The arrow shows the direction of axial tensile force acting on the lap shear test specimen. In Fig. 7 (b), the irregularities on the surface entrap the matrix of GFRP inside the aperture whereas the smooth surface of the metal in Fig. 7 (a) only shows the adhesion due to attractive forces between the substrate and the coating [10, 11].

The data provided in Table 2 comprehends that the tensile modulus tends to decrease for the composite bonded

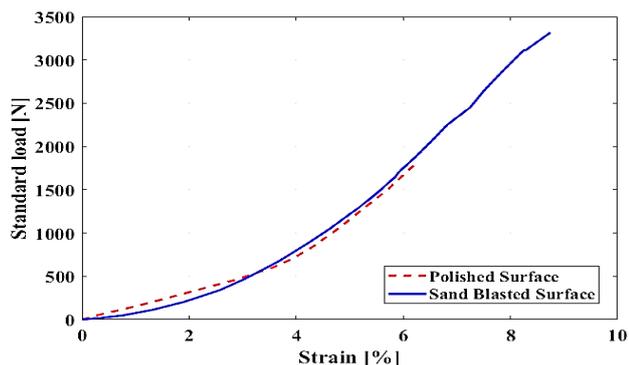


Fig. 6: Lap shear test for coating adhesion on mild steel with surface pretreatment

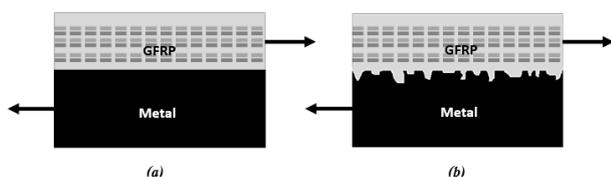


Fig. 7: Mechanism of adhesion for (a) polished (b) sandblasted surface in lap shear test with the direction of applied force

to the metal with irregular surfaces as compared to the smooth surface. This may be due to the surface roughness of the metal which may suppress the reversibility of elastic deformation. However, the tensile strength and the elongation before the detachment of the coating from the substrate increase as a consequence of polymer matrix entrapment which tends to hold the coating better for higher axial force leading to more plastic deformation.

CONCLUSIONS

Multi-layer composite of fiber-reinforced unsaturated polyester shows enhanced properties when tested for impact strength. The tensile strength, hardness, and flexural strength of the material are effective to be used as a coating over the substrate for underground tanks. The corrosion rate of the sample shows very positive results. No such corrosion occurs due to the presence of composite. No residue of corrosion was observed. The trend shown by the corrosion rate was only due to the exposed area which is the edges of the mild steel. Averaging out other drawbacks that can result due to its presence. This study can further proceed by testing it through a holiday test ASTM D5162 for discontinuity and crack propagation of coating over a substrate. This test can further clarify by giving proper knowledge of discontinuity, any pores present in the material which can result

in a medium of forming a corrosive layer on the metal. Moreover, Scanning Electron Microscopy (SEM) analysis can be used to characterize the metal surface with and without the coating in the effect of corrosion due to different environmental conditions. For a better knowledge of adhesive nature under different environmental conditions, ASTM D3762 is recommended. A steel wedge is inserted between the bonded composite on the steel plate and the initial crack length is noted. The assembly is then placed inside the environmental chamber where hot or wet conditions monitor the rate of crack growth also the rate of crack propagation under the effects of the environment. For safety concerns the composite can be tested for fire test for exterior structural stability and flame retardant may prevent the consequences.

Abbreviation

Symbol	Description
GFRP	Glass fiber reinforced with polyester
FRP	Fiber-reinforced plastic
UST	Underground storage tank
ASTM	American society for testing and materials
UTM	Universal testing machine
MS	Mild Steel
MEKP	Methyl Ethyl Ketone Peroxide
pH	Power of Hydrogen

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