CARBON FIBRE REINFORCED PVDF COMPOSITES

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Abstract
Unidirectional (UD) carbon fibre reinforced polyvinylidene fluoride (PVDF) was manufactured using a laboratory scale composite line with in-line atmospheric plasma fluorination of carbon fibre surface. The resulting continuous UD carbon fibre reinforced PVDF prepregs were used to fabricate reinforced thermoplastic pipes (RTPs) via filament winding method. Winding angle of ±55° was employed as a preliminary study. The impact of APF treatment of carbon fibres on the hoop tensile strength as well as stiffness of the RTP is presented. Improvements in the mechanical properties of the RTP indicates the ability of stress transfer between the fibres and the matrix through the interface is enhanced and this is due to the improved adhesion between the fibres and the matrix by incorporating APF on the fibre surface.

1 Introduction
Carbon fibres have been one of the most commonly used reinforcement in engineered composites over the past 40 years [1-3]. Exceptional mechanical properties as well as outstanding chemical stability make them an ideal material for use as reinforcement for polymers and, therefore, are widely used in structures and in load bearing applications including the flow lines for deep sea oil and gas exploration [4-6]. High modulus and excellent fatigue and chemical resistance are also some of the advantages of carbon fibres as compared to other reinforcements such as glass and aramid fibres. Though aramid fibres have the highest strength to weight ratio, they are not suitable for deep sea applications because they are very susceptible to water absorption and have poor compression properties when compared to carbon fibres [7-10].

The most widely used matrices for composites are polymers. This is because polymer materials are easy to process and do not require high pressure and temperature during composite manufacturing. Furthermore, polymers are known for their low density, and can be used either as solution or in molten state to impregnate the reinforcement, thus easing the manufacturing process [11]. This makes a low density composite with low manufacturing cost and diversity of material to choose from for different applications. For offshore application, the selection of the polymer matrix is based on the sustainability of the material to perform under environmental and mechanical loads, resistance to moisture and having a reasonable glass transition temperature (T_g) to make sure the polymer can withstand a reasonably wide temperature range during its service [12]. Polyvinylidene fluoride (PVDF), which is a fluorinated thermoplastic is widely used in the high purity semiconductor market as well as for the manufacturing of pipes, valves and ultrafiltration membranes [13]. As a fluoropolymer, PVDF exhibits not only great toughness but also a reasonable thermal performance. Besides that, PVDF has excellent chemical resistance, low permeability to gases and liquids and low water absorption (0.03%) which are the key parameters for deep sea oil and gas applications. Furthermore, in the oil and gas industry, PVDF has already been recognised and used as pipe liner especially where the material has to withstand highly corrosive fluids [14]. To exploit the full benefits such as inertness and other outstanding characteristics of PVDF, it has been reported previously that PVDF can be used as matrix in carbon fibre reinforced polymer composites [15, 16]. Although the mechanical performance of carbon fibre reinforced PVDF is relatively low as compared to aromatic polymer composites (APC2), however, studies conducted previously have shown that it is possible to improve performance of the composite by adopting atmospheric plasma fluorination (APF) of carbon fibres or by modifying the surrounding matrix by incorporating maleic anhydride grafted PVDF [16-18]. A preliminary study on the mechanical performance of reinforced thermoplastic pipes (RTPs) fabricated by filament winding of carbon fibre reinforced PVDF composite prepregs at ±55° angle onto a PVDF liner is presented and discussed.

2 Materials and testing methods

2.1 Materials

Commercially available high strength, unsized, but industrially oxidized polyacrylonitrile (PAN) based carbon fibres (Hexcel, AS4 12K) supplied by Hexcel Corporation (Duxford, Cambridge, UK) were used in this study. Kynar® 711 Polyvinylidene fluoride (PVDF) was used as the matrix material and was kindly supplied by Arkema (King of Prussia, USA). The surfactant used was Cremophor® A25 (BASF, Ludwigshafen, Germany). Gases used as feed gas for the atmospheric plasma fluorination were chlorodifluoromethane (Freon 22) and nitrogen (N_2) (BOC, London, UK). An unreinforced PVDF pipe (2” Schedule 80 x 6 m pipe) was purchased from Professional Plastics, Fullerton, California, USA and was used as internal liner for the composite pipe fabrication.

2.2 Manufacturing of unidirectional (UD) carbon fibre reinforced PVDF composite prepregs with inline atmospheric plasma fluorination (APF) modification of carbon fibres

The method used for the manufacturing of UD carbon fibre reinforced PVDF composite prepregs was a wet powder/slurry impregnation route. A spool of 12K AS4 carbon fibres was set under a tension of 100 g from a tension let-off unit (Izumi International, Greenville, SC) and was passed through a continuous atmospheric plasma treatment jet (FLUME Jet RD1004; Plasmatreat, Steinhagen, Germany) for the inline APF modification of the carbon fibres. A detailed description of APF treatment on carbon fibres can be found in [19]. The detailed of the manufacturing process can be found in Ref [20]. The UD composite prepregs were manufactured using three different manufacturing speeds; 1 m/min, 0.75 m/min and 0.33 m/min to study the effect of different fluorine contents on the fibre surface when subjected to APF on the mechanical properties of the composites produced. During the manufacturing process, the polymer powder in the impregnation bath is consumed by the continuous fibre tow, which leads to a potential variation in the composite’s fibre volume fraction, V_f, which is determined by the formula;

$$V_f = \frac{\rho_m W_f}{\rho_f W_m + \rho_m W_f} \tag{1}$$

where ρ and W corresponds to the density and weight and f and m are the fibre and matrix properties respectively (ρ_m = 1.78 g/cm^3, ρ_f = 1.80 g/cm^3 and W of 1 m fibre = 0.858 g). Therefore, to ensure a consistent fibre volume fraction of the unidirectional composite prepregs, the concentration of the impregnation bath has to be kept constant throughout the manufacturing process. This was achieved by addition of 50 ml of concentrated polymer suspension (20 wt%) at regular intervals. Only carbon fibre reinforced PVDF composite prepregs with V_f of 60 ± 2% were chosen for further characterisation.

2.2 Production of reinforced thermoplastic pipes

Reinforced thermoplastic pipes (RTP) were fabricated using a continuous filament winding technique. Pure (unreinforced) PVDF pipe (2” Schedule 80 PVDF) having an outside diameter of 60.4 ± 0.1 mm and average thickness of 5.75 mm was mounted and secured onto a steel mandrel using a heat resistant flash tape. This pipe served as the internal liner for the composite pipe. The UD composite prepregs were then passed through a series of horizontal pins and onto a PTFE roller exiting into an angle control unit before it was secured onto the pure PVDF liner by direct heating of the prepregs on the PVDF liner. The winding process was controlled using a filament winding machine (Type: LW11-50/200 Retrofit, Waltritsch & Wachter GmbH, Bodnegg-Rotheidlen, Germany). The winding angle and speed were set to ±55° and 25 mm/s, respectively. The filament winding process was continued until the desired composite wall thickness (~3.5 mm) was obtained.

2.3 Mechanical characterisation of RTP

2.3.1 Hoop tensile tests of RTP sections

Hoop tensile tests were conducted on pipe sections by using the split disk method according to ASTM D2290 [21]. A pipe section having an outside diameter of 65.0 mm, a thickness of 8.5 mm and a width of 25 mm was mounted into a self-aligning split disk test fixture. The composite ring was loaded into the jig without drilling a reduced section according to the standard [21]. Hoop tensile tests were carried out in an Instron 5581 (Instron, High Wycombe, Buckinghamshire, UK) equipped with 50 kN load cell. The cross head speed was set to 12.5 mm/min and the specimen was loaded until failure. The apparent hoop tensile strength σ of the RTP section was calculated based on the equation below:

$$\sigma = \frac{P_{\max}}{(b_1 d_1 + b_2 d_2)} \tag{2}$$

where P_{max} is the maximum load at failure, b_1 and b_2 are the width of the specimen at the midpoint of disks which are located 180° apart, d_1 and d_2 are the thickness of the specimen at the midpoint of disks which are located 180° apart. The test was conducted on at least five specimens to obtain a statistically significant average and the errors presented are standard deviations.

2.3.2 Compression tests of RTP sections

The compressive properties of RTP sections were determined from external load-deflection characteristics of the composite pipe under parallel plate loading according to ASTM D2412 [22]. This test method was used to determine the pipe stiffness and stiffness factor which can be used for engineering design. A RTP section of the same dimensions as stated in section 7.2.5.1 was placed between two parallel plates. The compression test was carried out at a crosshead speed of 12.5 mm/min in an Instron 5581 (Instron, High Wycombe, Buckinghamshire, UK) equipped with a 50 kN load cell, until the specimen deflection reached 30% of the average inside diameter of the composite pipe. The pipe stiffness *PS* and stiffness factor *SF* were calculated as follows:

$$PS = \frac{F^d}{\Delta y} \tag{3}$$

$$SF = 0.149 r^3 \cdot PS \tag{4}$$

where F^d is the load per unit length at a specific deflection (N/mm) (in this case, at 30% deflection), Δy is the change in the inside diameter of the specimen in the direction of load (mm) and r is the internal radius of the pipe specimen (mm). The percentage of pipe deflection, P can be calculated as follows:

$$P = \frac{\Delta y}{d_i} \times 100 \tag{5}$$

where d_i is the initial inside diameter of the specimen (mm). The stiffness factor can also be written as a function of the materials flexural modulus E (GPa) and wall thickness of the pipe t (mm);

$$SF = EI = E \cdot \frac{t^3}{12} \tag{6}$$

At least 5 specimens were tested to obtain a statistical average pipe stiffness and stiffness factor. The errors presented are standard deviations.

3 Results and discussion

It has been shown previously that the manufacturing speed of 1 m/min, 0.75 m/min and 0.33 m/min corresponds to retention times of 0.6, 0.8 and 1.8 min, respectively, in the active zone of APF jet [17, 23]. It has also been shown that the amount of fluorine functional groups present on the fibre surface increased with the retention time. Table 1 summarises these findings.

Table 1 Line speed, retention time and fluorine content of fibre exposed to inline APF modification

Line speed (m/min)	***Retention time (min)***	***F (at.-%)***
1.00 (untreated)	0.6	-
1.00	0.6	1.7
0.75	0.8	2.8
0.33	1.8	3.7

3.1 Mechanical performance of RTP

The winding angle is the major dominating factor influencing the mechanical performance of RTPs [24]. Higher winding angle contributes to higher hoop modulus and, therefore, can resist higher buckling load when the RTP is subjected to external pressure. Lower winding angle on the other hand contributes to higher axial strength and modulus [25]. A winding angle of ±55° was chosen for this preliminary study, as it is widely used and has been established as the optimum winding angle for a tubular section where the hoop-to-axial stress ratio can be as high as 2:1 [25, 26]. The methods chosen for characterising the RTPs fabricated were hoop tensile strength determined using a split disk test and compression determined using parallel plate loading tests. According to the ASTM D2290 standard, the split disk test fixture may impose a bending moment at the split during the test and, therefore, the results do represent the apparent tensile strength rather than the true tensile strength of the material. When applied to a composite structure such as used in this study, it is more complex because the composite pipe was made using a ductile PVDF liner and an outer layer consisting of an UD carbon fibre reinforced PVDF that is wound around the liner at an angle of ±55°. The apparent tensile strength of the neat PVDF pipe and RTPs fabricated using UD composite prepregs manufactured at different processing speeds which correspond to various degrees of fluorination on the carbon fibre surface are presented in Table 2. The apparent tensile strength of the pure PVDF pipe was determined to be 52.9 ± 0.3 MPa, which is similar to the tensile strength of Kynar® 711 PVDF as quoted by the manufacturer[1] as well as previously reported results [17]. By adding a 3 mm thick layer of ±55° carbon fibre reinforced PVDF around the pure PVDF pipe, the apparent hoop tensile strength increased by 8% to 57 ± 1.2 MPa.

Table 2 Apparent tensile strength of pure PVDF pipe and RTPs fabricated using UD composite prepregs manufactured at different degrees of fluorine content on fibre surface

Specimen	***Apparent tensile strength (MPa)***
Pure PVDF	52.9 ± 0.3
Untreated CF/PVDF	57.2 ± 1.2
APF treated CF/PVDF (1.7 at.-% fluorine content on CF surface)	58.7 ± 2.0
APF treated CF/PVDF (2.8 at.-% fluorine content on CF surface)	59.7 ± 1.0
APF treated CF/PVDF (3.7 at.-% fluorine content on CF surface)	63.0 ± 2.0

Figure 1 RTP consisting of a PVDF liner reinforced with layers of ±55° carbon fibre reinforced PVDF after subjected to split disk tensile test

The effect of APF treatment of the carbon fibre on the apparent tensile strength of the composite structure was also quantified. As expected from previous results, the improvement in the apparent hoop tensile strength is not significant if the PVDF composite contained carbon fibres with a low degree of fluorination, i.e. carbon fibre with surface fluorine content of 1.7 at.-%, the apparent hoop tensile strength of the RTP was 58.7 ± 2.0 MPa. However, it is notable that the apparent hoop tensile strength improved up to 19% to 63.0 ± 2.0 MPa when

[1] Kynar® 710 Homopolymer, Matweb. Link in: http://www.matweb.com/search/DataSheet.aspx?MatGUID=7378d6bf9bf84f2b8dcc1f49d40eeb44. Last accessed on 03.03.2012

carbon fibre reinforced PVDF containing carbon fibres with surface fluorine content of 3.7 at.-% was used. The reason for this improvement of the tensile strength is the enhanced interfacial adhesion between fluorinated fibres and PVDF matrix [15, 17, 18, 27] resulting in an enhanced load transfer between the fibre and the matrix. The stiffness factor, $E{\cdot}I$ at 10% deflection of the pure PVDF pipe and PVDF pipes reinforced with carbon fibres with varying degree of fluorination is presented in Table 7.2. The stiffness factor of the pure PVDF pipe was 39 ± 2.0 μN/m. Based on this result, the PVDF flexural modulus can be calculated using equation 12, and was found to be 2.3 GPa. This value is comparable to the Young's modulus of Kynar® 711 PVDF material[1]. The stiffness factor of the RTP made with as-received AS4 fibres was found to be similar to that of the pure PVDF pipe. It was reported that the flexural stiffness of RTPs are usually comparable with unreinforced systems [28] and, therefore, the reinforcement does not have any effect on the stiffness factor of the overall structure. Furthermore, it is difficult to calculate the flexural modulus of the structure as it is made of two different materials (pure PVDF liner and carbon fibre reinforced PVDF). However, by introducing fluorine onto the carbon fibre surface, the pipe stiffness factor increased up to 15% to 43 ± 0.6 μN/m when carbon fibres with surface fluorine content of 1.7 at.-% was used to reinforce the PVDF pipe. Further increase in the degree of fluorination does not have any influence on the composite pipe stiffness factor as the values observed were within the error (Table 7.3). However, it can be seen that APF does have a positive impact on the stiffness factor of the RTP. This observation indicates that the composites made with fluorinated fibres allow for better utilization of fibres by enhancing the stress transfer and, therefore, able to withstand higher stresses when subjected to external load. During the test, no rupture, cracking, or crazing was observed on all the specimens even after being compressed of up to 50% of the internal diameter of the pipe.

Table 3 Stiffness factor, $E{\cdot}I$ of pure PVDF pipe and RTPs fabricated using UD composite prepregs manufactured at different degrees of fluorine content on fibre surface

Specimen	*Stiffness factor, E·I (μN.m)*
Pure PVDF	38.8 ± 0.5
Untreated CF/PVDF	38.7 ± 0.3
APF treated CF/PVDF (1.7 at.-% fluorine content on CF surface)	43.2 ± 0.7
APF treated CF/PVDF (2.8 at.-% fluorine content on CF surface)	45.2 ± 0.3
APF treated CF/PVDF (3.7 at.-% fluorine content on CF surface)	43.6 ± 1.0

Summary

The search for a strong, lightweight material to replace heavy and corrodible alloy pipes used for the exploration of deep-water offshore oil fields has motivated the oil and gas industry over the past few decades. PVDF, a polymer approved by the oil and gas industry to be used as internal liner in offshore pipelines and risers, has yet to be utilised completely. However, due to the inertness of PVDF, adhesion to carbon fibre has always been a challenge. This is tackled by fluorinating the carbon fibre surfaces in APF which was proven to improve the interfacial adhesion between the fluorinated fibres and PVDF. To study if the improvements observed in single fibre model composites and composite laminates reported previously are translated into a composite structure, RTPs were fabricated by filament winding UD carbon fibre reinforced PVDF prepregs with a winding angle of ±55° onto a pure PVDF liner. Unreinforced PVDF pipe and the fabricated RTPs were subjected to hoop tensile and compression tests. The apparent hoop tensile strength improved up to 18% for RTP made with carbon fibre reinforced PVDF containing APF treated fibres with surface fluorine content of 3.7 at.-% as compared to as-received fibres. Similar improvement was observed in the stiffness factor of RTP when the composite pipe structure was loaded under compression. These enhanced mechanical properties show that APF treatment of carbon fibres can tailor the fibre-matrix interface leading to better stress transfer between the fibres and matrix leading to improvement in the overall composite performance.

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