STUDY OF MWCNTS FILLED TOUGHENED EPOXY FOR ANCHORING COMPOSITE TENSILE ARMOURS INSIDE THE END FITTING OF FLEXIBLE RISER

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ABSTRACT

The use of composite and nanocomposite materials is a growing trend in many industries such as aerospace, automotive, civil construction and energy. For many applications, the attachment between structures for efficiently transferring static and dynamic loads is a difficult problem to solve, especially for products which operate for long periods of time under extreme environments with corrosive fluid and high temperature. In the oil and gas segment, for instance, a common technique used for anchoring the tensile armours of flexible riser within the end fitting is through an embedded epoxy resin since it provides good chemical resistance and stable mechanical performance. Even though, cracks and defects can arise in the epoxy block during operations and end fitting mounting at resin curing step, and such cracks could affect the anchoring performance, in particular for composite armours. In this context, this work deals with the understanding of carbon fibre composite armours adhesion behaviour with an epoxy based matrix filled with multi-walled carbon nanotubes (MWCNTs) with a focus on improving the epoxy mechanical properties and its performance in adhesion. Mechanical characterization tests were carried out with referenced and filled epoxies to evaluate the gain of strength and modulus under tension and compression. The delamination toughness is also characterized in order to evaluate the resistance of the bonding structures. Test results confirmed an improvement in some epoxy mechanical properties and delamination toughness although MWCNTs dispersion may by optimized since some agglomerates were found by SEM analysis.

ABBREVIATION

CFA	Carbon fibre armour
EF	End fitting
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DWCNT	Double-walled carbon nanotube
MMB	Mixed-Mode Bending
MWCNT	Multi-walled carbon nanotube
SEM	Scanning electron microscopy
SWCNT	Single-walled carbon nanotube
UDW	Ultra-Deep Water

1 INTRODUCTION

Flexible risers are multi-layered pipelines that connect offshore platforms to submarine wells for transferring oil, gas and water [1]. Each layer has its functions such as collapse resistance, leak-proofness, and supporting pressure, static and dynamic loads, for instance. One particular layer so called tensile armours comes in pairs and is responsible for withstanding the axial loads induced by flexible weight, movements of the platform and end cap effect. Figure 1 presents the most common layers used in a flexible riser.

For past years in the oil and gas subsea industry, solutions with composite materials are becoming more often for many components especially due to the increase of depth of the offshore fields, commonly called Ultra-Deep Water (UDW) fields. The tensile armours, for instance, are usually made of carbon steel. However, since it generates excessive tension to the pipe due to their weight, the use of a lighter but resistant material is attractive. The composite material studied for these armours is based on carbon fibre, called the Carbon Fibre Armour (CFA) [2]. The main advantage of this type of wire is precisely the specific mechanical strength when compared to carbon steel.

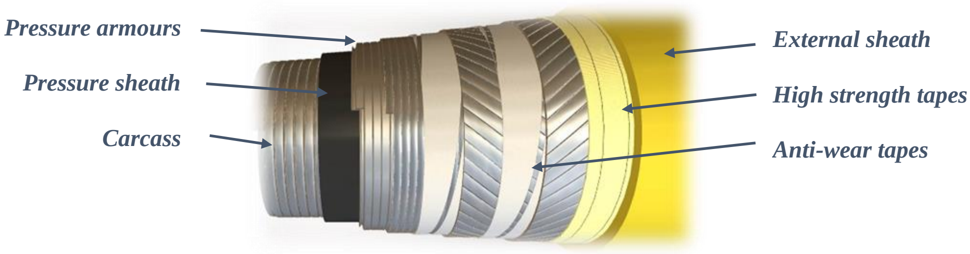


Figure 1: Typical illustration of flexible pipe layers.

Nevertheless, the CFA solution for risers brings some challenges for anchoring it at the extremity of the riser, inside the End fitting (EF), Figure 2. In this case, the behaviour considered for anchoring the CFA is by adhesion with the epoxy resin, while the approach used for steel armours is friction [4, 5]. With the CFA bonded to epoxy, a new composite is formed where the CFA acts as reinforcement and the epoxy as matrix, which means that the epoxy's integrity and mechanical properties impact directly on the performance of this new composite.

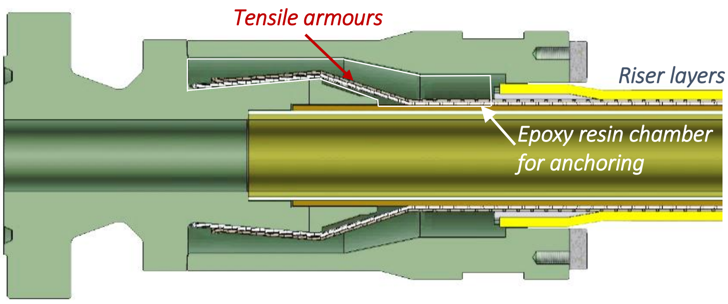


Figure 2: Typical illustration of flexible pipe EF with tensile armours [6].

Incorporating carbon nanotubes (CNTs) fillers for toughening the epoxy matrix tends to provide an improvement of the anchoring system. Indeed, this method has been widely studied as reinforcement of epoxies [7, 8, 9]. They are normally synthetized with one, two or multi-layers, known as single walled (SWCNTs), double walled (DWCNTs) and multi-walled (MWCNTs), respectively. The CNT geometry offers a high ratio of surface area by weight, high electrical and thermal conductivity, and excellent mechanical properties, which may improve all these characteristics of a polymeric matrix [10, 11]. Furthermore, its combination with epoxy matrices can improve the adhesive performance as confirmed in references [12, 13]. However, CNTs have also setbacks that must be taken into account such as cost and difficulty of processing. To ensure the homogeneous dispersion and good bonding to the matrix, some techniques are required. High shear mixing like three rolls machine and ultrasonic

bath for dispersion are some of the methodologies used [8]. The glass transition temperature is another parameter that can be impacted by nanotube filling. Some authors already confirmed an increase of 4% [14] and 24% [15] with 1.0%wt of MWCNTs, although the gain is not always assured depending on concentrations and type of CNTs, dispersion and cure processes.
The present work studies the relation between the CFA adhesive resistance and the improved epoxy matrix. The composite armour is considered as a constant parameter with its pre-established data. The matrix, on the other hand, has its mechanical behaviour studied, aiming to improve the final composite system. Small-scale tests are performed with the referenced and toughened epoxies, and with the CFA-Epoxy system.

2 EXPERIMENTAL STUDY

In order to characterize the gain of mechanical properties of the filled epoxy, a first batch of tensile [15] and compressive [16] small-scale tests were carried out with toughened and referenced epoxy samples. Then, delamination toughness by double cantilever beam [17] was performed with CFA-epoxy systems, varying only the epoxy properties by toughening with nanotubes.

The CFA material used was a carbon fibre composite supplied by TechnipFMC and the epoxy system chosen was a proprietary supplier formula. Two types of nanotubes, MWCNTs and a proprietary supplier modified *m*-MWCNTs, with aspect ratios from 330 to 1500 were used for toughening. Furthermore, two different concentrations were considered, 0.5%wt and 1.0%wt.

Knowing that a good dispersion of MWCNTs is very important to guarantee a homogenous sample material, a high shear mixing three rolls machine was used for one hour of mixing and a gap of 5µm.

To mitigate defects in samples, two vacuums were applied during thirty minutes at ambient temperature prior and just after applying the hardener. The second vacuum step was possible due to the high pot life offered by the chosen epoxy. Then, the compounds were placed in the moulds and cured at 60°C during twenty hours. The non-modified epoxy samples followed the same steps except for the three rolls machine.

Five samples were prepared for each test. The machine used for the tensile tests was the *Instron 4206*, with a 100kN static load cell, ±2.5mm travel extensometer and speed 1.5mm/min. For the compressive tests, an *Instron 4482* machine was used with a 30kN static load cell, and same travel extensometer and speed. The delamination toughness tests were performed with a MMB device, with speed 0.5mm/min.

3 RESULTS AND DISCUSSION

The results found from the first mechanical tests already confirmed a slight improvement of epoxy mechanical properties and also CFA-epoxy adhesion system. Table 1 summarises the small-scale tests performed with the toughened and referenced epoxy matrix, and with CFA-epoxy system (Delamination toughness test) for 1%wt *m*-MWCNT toughened epoxy. The results found in tension with the referenced epoxy were coherent with previous studies [19].

Test	Property	Ref. epoxy	0.5%wt MWCNT	0.5%wt *m*-MWCNT	1.0%wt *m*-MWCNT
Tensile (MPa) $_{epoxy}$	Strength	75.2±0.9	77.8±1.2	72.0±0.9	76.4±0.8
	Modulus	2950±75	2900±30	3000±30	3350±100
	Strain	5.4%±0.5	5,0%±0.3	5.9%±0.8	5.3%±0.6
Compressive (MPa) $_{epoxy}$	Strength	97±0.9	100±0.8	98±0.0	102±0.7
	Modulus	2300±130	2480±150	3110±80	3360±180
Delamination Toughness $_{CFA\text{-}epoxy}$	G_c (J/m^2)	150±24	-	-	178±19
	G_{IIc} (J/m^2)	28±5	-	-	34±4

Table 1: Summary of test results with referenced and MWCNTs toughened epoxies, and CNT concentrations of 0.5%wt and 1.0%wt.

According to the table, although the addition of 0.5%wt MWCNTs did not provide expressive changes on epoxy properties, the composites with 1%wt *m*-MWCNT caused an increase in some mechanical properties. The Young's modulus and the Delamination toughness, which are parameters quite important for transferring and withstand the CFA loads in the anchoring system, reached nominal improvement of 14% and 20%, respectively. Moreover, no significant brittle behaviour of the epoxy was found by adding CNTs, especially *m*-MWCNT. Regarding the 0.5%wt MWCNT and 1.0%wt *m*-MWCNT, the elongation had small decrease and the tensile and compressive strengths remained almost the same, still with a small gain. In addition, the compressive modulus increased 46% with 1.0%wt *m*-MWCNT.

Figure 3 presents the tensile stress-strain curve (a) and the increase of Delamination toughness, in Mixed-Mode (1 and 2) and Mode 2, by adding 1.0%wt *m*-MWCNT (b).

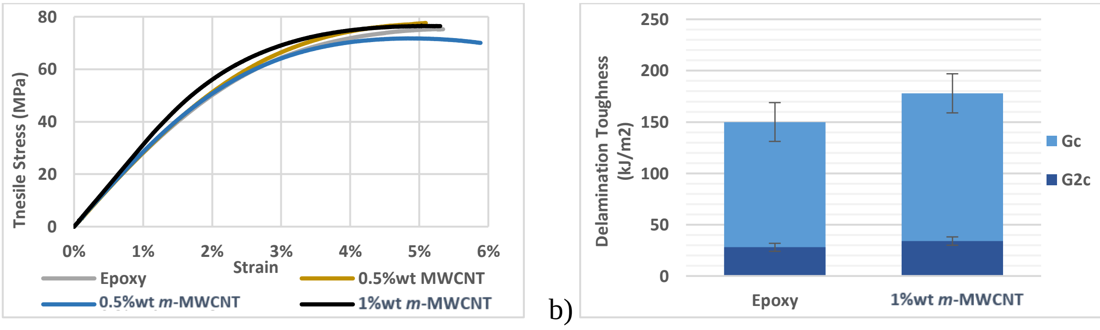


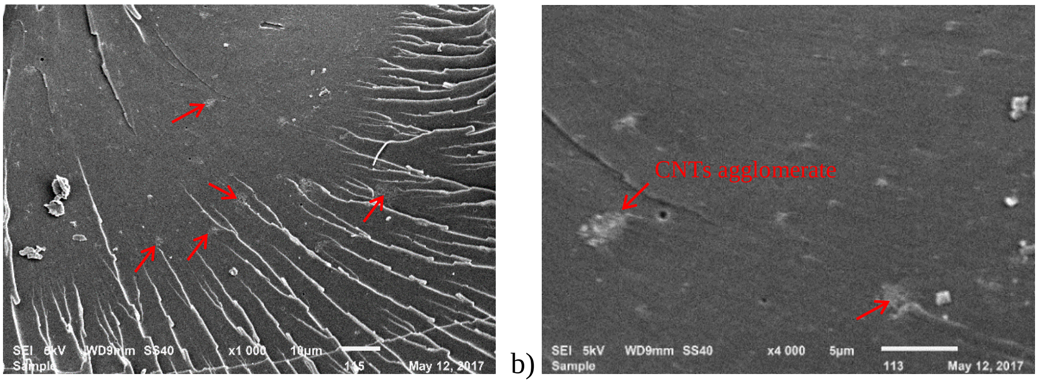
Figure 3: a) Stress-strain curves; b) Delamination toughness in Mode 2 and Mixed-Mode 1 and 2 of system CFA-epoxy, with non-modified and toughened 1%wt *m*-MWCNTs epoxies.

Since the concentration of 1.0%wt showed tougher performance offering higher modulus without losing elongation and strength, higher concentrations of MWCNTs could be tested in the future in order to increase further the modulus until it starts becoming brittle. In this case, fracture toughness tests [19] should also be assessed.

Although positive results have been reached, they were not as high as expected, if compared to the gain of 59% in Young's modulus in reference [19], for example. Indeed, there are several parameters that may impact on final results which must be studied more deeply in the future such as: the type of epoxy, hardener and MWCNTs; nanotubes length and aspect ratio.

Some non-negligible deviation, especially in strain from tensile tests and in Delamination toughness, have been found between the five samples tested. It could be linked to the repeatability of the protocol for preparing the samples. Besides, the degree of cure is one of the parameters that could be evaluated by DMA and/or DSC in order to verify if the time/temperature considered for curing was enough or even to check if samples with CNTs should be subjected to higher temperatures or longer duration. The poorer behaviour of the 0.5%wt *m*-MWCNTs sample in tension, for instance, or even the other results that did not reached higher improvements could be explained by the lower degree of cure.

The dispersion of CNTs is another important factor that could be reassessed. Figure 4 presents SEM images taken from 0.5%wt and 1%wt *m*-MWCNTs samples.



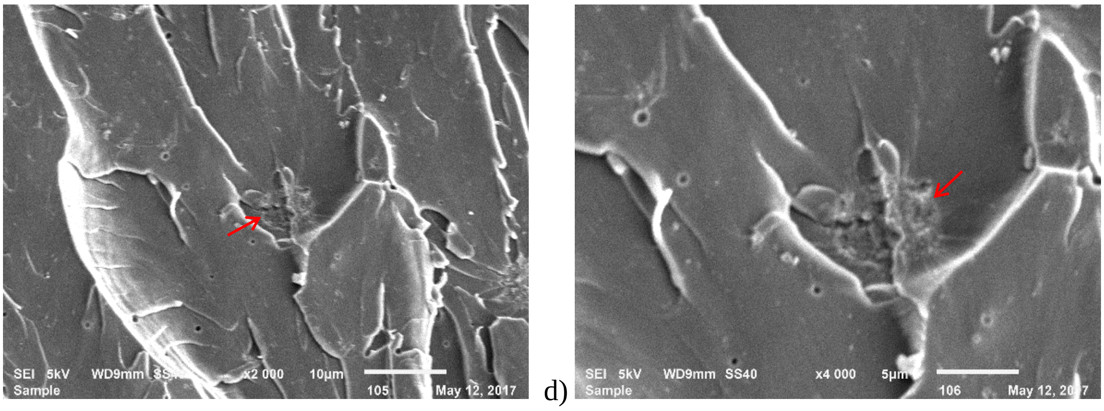
c) d)


Figure 4: SEM images showing dispersion of CNTs in the epoxy matrix samples: a) x1000 from 0.5%wt *m*-MWCNT; b) x4000 from 0.5%wt *m*-MWCNT; c) x2000 from 1%wt *m*-MWCNT; d) x4000 from 1%wt *m*-MWCNT.

In Fig.4a, although it presents a relatively good dispersion, several CNTs agglomerates were found. Fig.4b shows some of them zoomed. Inspecting the 1%wt *m*-MWCNTs sample, it was more difficult to find agglomerates, nevertheless Figures 4c and 4d show CNT agglomerates with approximately 5µm in diameter, which is the same gap (minimum feasible from the three rolls machine) used for the dispersion.

Even if smaller gaps were possible in the three rolls machine, its setup (speed, gap and duration) may impact not only on the homogeneity of the dispersion but also on their structural integrity, that is, depending on the configuration, it could break some of nanotubes and the aspect ratio would be compromised. An option that could be considered for enhancing it is to combine the high shear mixing with an ultrasonic exposition.

4 CONCLUSIONS

The preliminary tests with the MWCNTs filled toughened epoxy already showed an improvement of mechanical properties, such as epoxy's tensile and compressive modulus and the delamination toughness of the system CFA-epoxy, particularly for the composites with 1%wt *m*-MWCNT. The strengths remained mostly unchanged and there was no significant decrease of strain especially with the modified nanotubes. Therefore, it confirmed a tough matrix behaviour and a potential solution for increasing the anchoring resistance of the system if additional tests and the parameters like CNTs dispersion, cure protocols and epoxy family are deeply assessed. Besides, higher concentrations of *m*-MWCNTs, 2%wt for instance, could be evaluated since 1%wt *m*-MWCNT was still tough.

SEM analysis showed some CNT agglomerates even though matrices had relative good homogeneity in CNTs dispersion. Adding an ultrasonic bath step besides the three rolls machine could be an option for reducing these agglomerates and reaching better mechanical results.

Although the present work enabled an introduction of characterization of the material properties and adhesion toughness to the CFA, future tests such as fracture toughness with epoxy and lap shear [21] with CFA-epoxy system shall be performed to confirm the material improvement. It is also important to perform an exhaustive campaign of straight pull-out testing with CFA-epoxy system in next works with the referenced and toughened epoxy in order to consolidate the suggested system.

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