THERMOPLASTIC MATRIX COMPOSITES FOR UNDERWATER APPLICATIONS

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ABSTRACT

Thermoplastic matrix carbon fibre composites offer considerable potential for underwater applications. There are various material options but there are questions concerning the compression behaviour and water sensitivity of the less expensive polymers (polyamides) for these applications. The aim of this study is to assess whether thick carbon/polyamide cylinders produced by tape placement could provide a low cost solution for underwater pressure vessels, by examining these two aspects. The influence of sea water immersion was examined first, in order to propose a diffusion model so that the water profile could be determined. Compression properties were then measured for dry and wet specimens. Before aging, values were comparable to carbon/epoxy, around 1400 MPa, but these were reduced to around 600 MPa in fully saturated specimens. Pressure vessel implosion tests on preliminary tube samples indicated an implosion pressures around 200 bar for 10mm thick 120mm diameter carbon/polyamide cylinders, but this should be increased by optimized manufacturing conditions. For deep sea applications alternative carbon/PEEK materials have been shown to provide the required implosion resistance.

1 INTRODUCTION

More than 95% of the oceans remain unexplored. With an average depth of over 3800 meters, it is necessary to design devices that are able to withstand high hydrostatic pressures. Also, the lighter these pressure vessels are the more equipment and measuring instruments they can carry, so composites have been used underwater for many years. The main industries concerned today are oceanography, military, and offshore oil and gas. For all these applications the principal manufacturing technique is filament winding, which enables cylindrical tubes to be manufactured in a semi-continuous process at low cost.

The use of composites for pressure hulls of underwater vehicles and submarines has been an ongoing research topic for many years, since early work in the UK by Smith and colleagues in the 1970's [1]. They focused on glass reinforced thermoset composites, but subsequently their work was extended to carbon fiber reinforced thermosets in the 1990's as the potential of these materials for weight saving became apparent. For some unmanned submersibles (autonomous underwater vehicles) composites are used for the pressure resistant hulls. Two examples are the autonomous underwater vehicles AUTOSUB [2] and the AUSS [3]. Design of the former began in 1988 for the UK Natural Environment Research Council. Extensive system development took place over 5 years and the first complete vehicle was built between October 1995 and May 1996. AUTOSUB undertook its first autonomous mission in July 1996, it is 7 meters long and has a depth limit of 1600 meters.

The AUSS (Advanced Unmanned Search System) vehicle, developed for the US Navy in the 1980's, was designed to operate down to 6000 meter depth. It is 5 meters long, 0.8 meters in diameter, and weighs 1.2 tons. The center section is a cylindrical carbon/epoxy pressure hull (wound at $0°/90_2°$) with titanium hemispherical ends. The hull provides the central structure and all its buoyancy, no syntactic foam buoyancy is used.

Large quantities of composites are used on military submarines. While many of the details are confidential, some published information is available [4,5]. Lemière [4] relates that a composite workshop was first set up in 1955 at the Cherbourg dockyard, and external decks of conventional French submarines were made of glass reinforced composite from 1974. For the "Triomphant", a missile-launching nuclear submarine, composite applications include the sonar dome, the propulsion unit and fins, and the outer deck. The sonar dome, in thick monolithic laminate, is several meters in diameter and produced using a vacuum bag technique from 120°C cure prepreg. Sandwich materials are used for external deck surfaces. These represent 50% of the wetted surface (1200 m²) and are made of glass/epoxy 120°C cure prepreg facings on syntactic foam core. However, the structural hull is still metallic.

Various US Navy and ONR (Office of Naval Research) programs and several European projects have resulted in a solid database of test results from implosion studies on a range of materials and geometries [e.g. 6-9]. Other more academic studies have included buckling [10,11], failure envelope determination [13-15], post-buckling behavior [16], and studies of winding angles [17].

1.1 Thermoplastic composites

There is an increasing number of thermoplastic matrix polymers available on the market (PP, polyamide, PPS, PEEK…), which offer possibilities for forming by local heating, attractive mechanical properties, good environmental resistance and the potential for end of life recycling. More ductile and reparable by melting, they offer a real potential for greatly improved devices. From a scientific point of view, most of the previous studies conducted on these materials were focused on aircraft structures, i.e. thin structures, and several studies have made connections between manufacture and microstructure [18,19]. Results from implosion tests on thermoplastic composite cylinders are rarer. A study in the USA on carbon/PEEK was described by Gruber et al [20]. At IFREMER studies were performed from 2000 onwards, to examine different thermoplastic matrix polymers for cylinders [21]. These tubes were supplied by American companies, first small diameter (55mm, 6mm wall thickness)) then larger (175mm diameter, 20mm thick). Two were retained for hydrostatic pressure testing, carbon/PEEK and glass/PEI. The former were very promising, implosion pressures similar to those for carbon/epoxy were obtained, while the latter suffered from poor manufacturing quality (high porosity) and imploded at much lower pressures than glass/epoxy of similar geometry.

1.2 Applications

The use of composite cylinders for oceanographic containers has been developed for many years. At IFREMER these materials have been employed for various prototypes. The first application in the 1990's was the SAR magnetometer, a 100mm diameter glass fiber reinforced tube. In the GEOSTAR project 55mm diameter glass/epoxy tubes were used as buoyancy units at 4000m depth. Composites were also considered for the instrumentation protection in the ANTARES neutrino telescope project, and some tests were performed at sea in 2500 meters water depth [22], but titanium alloy was finally adopted.

Another application is the casings of autonomous ocean profilers. These are tubes containing sensors which follow ocean currents at different depths taking measurements (temperature, salinity…) and rise to the surface periodically to send the data. They then return to their programmed depth. At shallow depths (2000 meters) aluminium alloy was used, but for 3500 meters depth the recent DEEP ARVOR project has resulted in the development of a carbon/epoxy profiler, Figure 1. This is currently undergoing sea trials.

Figure 1: Deep Arvor carbon/epoxy profiler

There are also several composite applications in the offshore oil and gas industry. These are not the main aim of the present project, but it should be noted that considerable work has been performed on long tubular composites both for risers and other flow-lines. Early work by IFP and Aerospatiale [23] in the 1980's was followed by various other projects over the last 25 years [24-27] to develop thermoset composite tubes with metal liners, and the publication of guidelines by the DNV [28]. Other groups have focused on thermoplastic matrix composites, in particular the Dutch company Airborne [29] which supplies down-lines for sub-sea intervention with various thermoplastic polymers.

2 PROJECT OBJECTIVES

The aim of the present study is to investigate the relationships between manufacturing, microstructure and wet compression properties of thermoplastic composites, Figure 2. In this first part of the project particular emphasis was placed on carbon/polyamides. These are attractive as they are much less expensive than high performance matrix polymers such as PEEK, but it is not yet clear to what extent their compression behaviour in the presence of water will limit the operating depth of an underwater pressure vessel. The project aims to determine this.

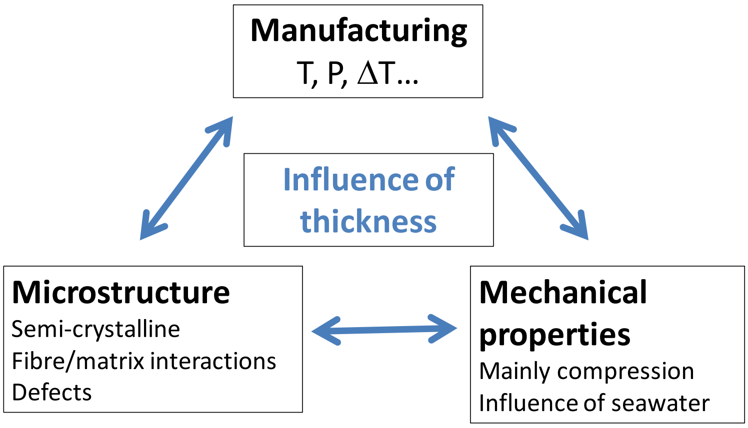

Figure 2. Schematic overview of project.

In order to achieve this both compression moulded plates and tape laid cylinders have been studied, all manufactured from the same carbon/polyamide prepreg. Polyamides 6 and 12 have been studied. The study of plates enabled large numbers of specimens to be produced, allowing manufacturing conditions to be evaluated and tests to be optimized. A compression moulding press at the IUT Composite facility in Brest was employed to produce the plates. Aging in natural sea water was performed at IFREMER in Brest. Cylinders were manufactured on a dedicated facility at the CETIM in Nantes, Figure 3.

Figure 3. Laser Assisted Tape Placement machine

Samples cut from plates were analyzed and tested, before and after seawater immersion. Analyses included X-ray micro-tomography and ultrasonic C-scan, to quantify defects, differential scanning calorimetry (DSC) and birefringence microscopy to examine microstructure, and mechanical characterization. Particular emphasis was placed on compression, using a compression bending test proposed by Fukuda [30], shown below.

The IFREMER hydrostatic pressure test facility in Brest was used for the cylinder implosion tests, as will also be described below.

3 INFLUENCE OF SEAWATER AGING ON COMPRESSION PROPERTIES

In spite of extensive work on aging of marine composites [e.g. 31, 32] there are few data relating seawater aging to compression properties of thermoplastic composites. Some results are available for carbon fiber reinforced PEEK tested in flexure after immersion for 2 years which show very little loss in properties [33], but few studies have examined carbon reinforced polyamides in water.

In order to establish how the behavior of a thick carbon/polyamide cylinder will change during immersion there are various points to consider:

- First it is necessary to determine the diffusion kinetics of seawater into the composite, and the extent to which these will change with both material microstructure and external pressure.
- Then the influence of seawater on compression behavior must be quantified.
- And finally the behavior of a cylinder under external pressure as water enters and properties evolve, must be assessed by appropriate coupled modeling and validated by testing.

3.1 Diffusion kinetics

Figure 4 shows one example of the weight gain of a carbon/polyamide sample immersed in continuously renewed natural seawater at 40°C.

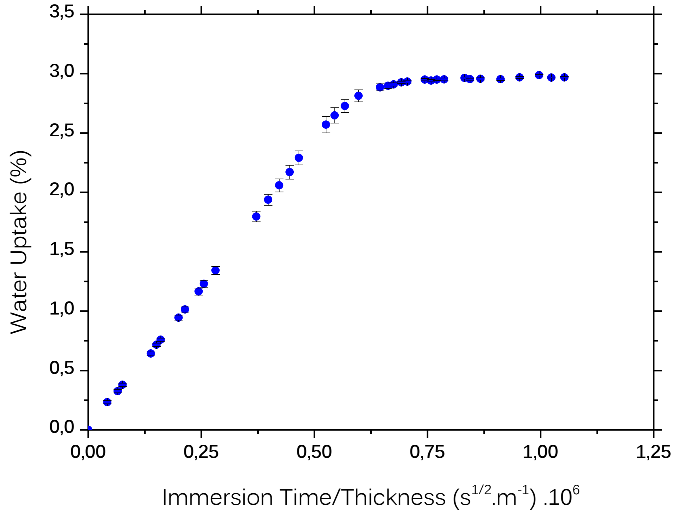

Figure 4. Diffusion kinetics, 40°C sea water carbon/polyamide 6, 2mm UD

The weight gain is Fickian. Similar plots were obtained at different temperatures, allowing the water profile in a 10mm thick tube at 15°C in seawater to be estimated. This indicates that it would take around 8 years to fully saturate a 10mm thick tube even at 25°C, while at deep sea temperatures (around 4°C) this would take over 50 years. This suggests that for an application such as a profiler, which drifts for around 2 years, the water ingress may not be critical.

3.2 Compression properties

It is notoriously difficult to obtain valid compression strength data on unidirectional composites. A range of standard tests exist but these tend to yield low values. After a preliminary study involving various test configurations the compression bending method was selected, Figure 5. This test was developed by Fukuda and colleagues [30,34] and provides a simple procedure to obtain compression properties.

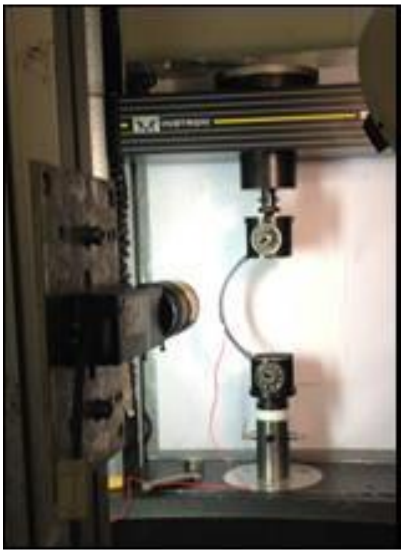

Figure 5. Compression test, strain gauged sample, camera to record shape change.

Compression tests were performed before and after saturation of specimens with natural seawater. Figure 6 and Table 1 show examples of results.

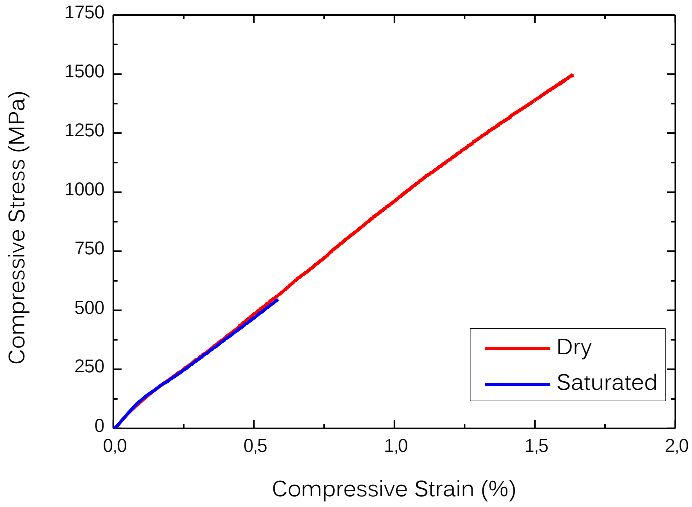

Figure 6. Compression stress-strain plots, before and after saturation

Test condition		Dry	Saturated
$\sigma_{1\ \text{comp. at failure}}$	[MPa]	1385 (101)	571 (37)
$\varepsilon_{1\ \text{comp. at failure}}$	[%]	1.53 (0.10)	0.62 (0.03)

Table 1. Compression strength results before and after saturation, mean (standard deviation) values.

These indicate that carbon/polyamide 6 composites can show good compression strength in the dry state. The values obtained here are significantly higher than those reported previously. For example, Botelho et al [35] found values below 400 MPa for carbon fabric reinforced polyamides.

After saturation in seawater these values drop, so if tubes made from these materials are to be used underwater it is essential to know how much water is present. Barrier coatings can be envisaged to slow down water ingress.

4 IMPLOSION OF CYLINDERS

This section describes results from some preliminary implosion tests on polyamide 6 and polyamide 12 cylinders. These were of 120mm inner diameter, 10mm wall thickness and 600mm long. It should be emphasized that these represent initial baseline test results designed simply to establish where the response of such cylinders was situated with respect to that of a commercial wet filament wound carbon/epoxy cylinder of similar geometry and fibre orientation tested at the same time. A major advantage of tape laying is that fibres can be oriented in all directions including at 0° and 90° to the tube axis. This allows optimization of the reinforcement directions, and work is underway to pursue this.

The three cylinders were first analyzed by C-scan, the two thermoplastic composites showed significantly fewer defects than the carbon/epoxy tube.

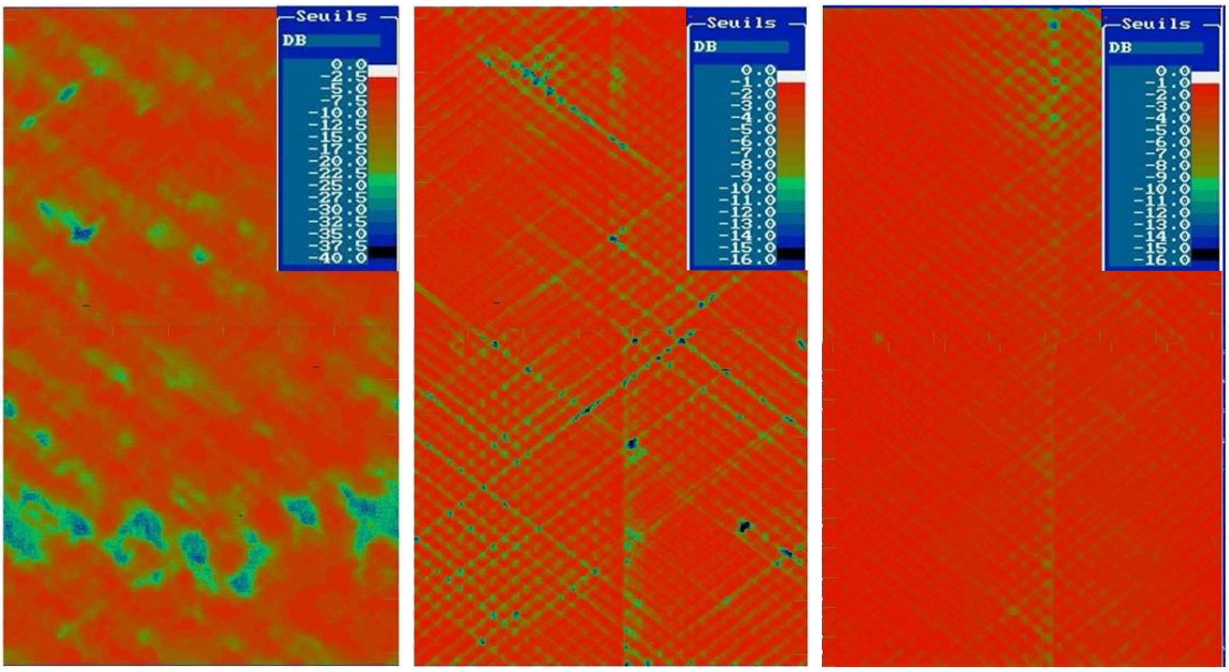

Figure 7. C-scan results (a) Epoxy 40 dB (b) PA12 16dB (c) PA6 16dB

Samples taken from the cylinders were examined using X-ray micro-tomography equipment at the Ecole Centrale de Nantes. Figure 8 shows one example. In Figure 8 the complete wall thickness is shown with some defects near the inner wall.

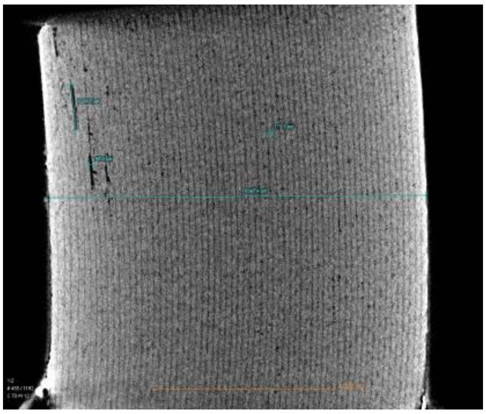

Figure 8. C-Scan Tomography, Carbon/polyamide 12 composite

End covers were bonded to the cylinder extremities in order to protect the ends and provide a suitable surface to seal the end plates. 12 strain gauges were bonded to the outer surface of each cylinder as shown in Figure 9, in order to be able to study the failure modes. An axial compression was performed before the implosion test to measure axial elastic properties.

Figure 9. Cylinder samples, under axial compression and before pressure test.

All cylinders were tested to implosion in a 2400 bar pressure vessel, Figure 10, with continuous recording of pressure, temperature and the 12 strain gauge measurements.

Figure 10. Cylinder being lowered into 2400 bar pressure vessel.

The results from these tests indicated that these first carbon fibre reinforced polyamide cylinders imploded at significantly lower hoop stress values than the reference carbon/epoxy (around one third). This was the result of a premature buckling failure induced by a slightly elliptical initial section. Further tests are underway to improve this.

Finally, an alternative to carbon/polyamide is carbon/PEEK. Various previous studies have indicated that this material can resist high external pressures [20,21,36], and offers another option for deep sea applications.

5 CONCLUSION

This paper describes results from a study to investigate the use of carbon fibre reinforced polyamides produced by tape placement for underwater applications. Three aspects have been investigated, the diffusion of seawater into these composites, their compression behaviour, and their response under external pressure. These materials are significantly less expensive than carbon/PEEK but few tests have been performed on them to date. First results indicate that good compression strength can be attained, further work is underway to optimize the pressure resistance of cylinders.

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