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Effect of sea water and humidity on the tensile and compressive properties of carbon-polyamide 6 laminates

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ABSTRACT

Thermoplastic matrix carbon fibre composites offer considerable potential for underwater applications. Various material options exist but there are questions concerning the tension/compressive behaviour and water sensitivity of the less expensive polymers (e.g. polyamides) for these applications. The aim of the current work is to model water diffusion and its effect on the mechanical properties of thick carbon fibre reinforced polyamide-6 composite cylinders immersed in sea water for deep sea applications. To provide the data for such a model, thin specimens (2 mm thick) have been aged under different humidity conditions and tested in tension and compression. As water enters the composite, a significant reduction in the laminate properties is observed. An empirical relationship that links matrix-dominated properties to water content is presented and can be used for modelling purposes.

1. Introduction

More than 70% of the oceans remain unexplored. With an average depth of over 3800 m, it is necessary to design exploration devices that are able to withstand high hydrostatic pressures. The lighter these pressure vessels are the more equipment and measuring instruments they can carry, so composites have been used underwater for many years [1]. The use of composites for pressure hulls of underwater vehicles and submarines has been an ongoing research topic for many years, since the early work in the UK by Smith and colleagues in the 1970s [2]. The use of glass and carbon reinforced thermoset composite materials for deep-sea applications needs a thorough understanding of the behaviour of these materials under hydrostatic pressure. However, the ability to predict the implosion pressures of such materials and under such loadings (bi-axial compression) is not an easy task, as was demonstrated by the results of the World Wide Failure Exercise [3].

Applications for thick thermoplastic cylinders for underwater applications are rarer, even though there is an increasing number of thermoplastic matrix polymers available on the market such as polypropylene (PP), polyamide (PA), polyphenylene sulphide (PPS), and polyetheretherketone (PEEK). They 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. Studies have been conducted in the USA on carbon/PEEK cylinders [4,5] and by the authors [6] and were found to be very promising as they imploded at comparable pressures to those of their carbon/epoxy counterparts. However, it is not clear to what extent the compressive behaviour of thermoplastic composites in the presence of water will limit the operating depth of an underwater pressure vessel, especially for carbon/polyamide 6 (C/PA6) composites. The latter are attractive as they are much less expensive than composites based on high performance matrix polymers such as PEEK.

The mechanical behaviour of composite materials has been extensively explored in the literature and their performance under tension loads is well understood. However, the behaviour of composite materials subjected to compressive loadings is less clear. Several studies have shown that composite compressive strengths are typically 50–70% of the tensile strength [7,8]. Compressive strength is widely acknowledged as one of the most difficult properties to measure in composite materials. Hart et al. [9] conducted round robin tests within seven laboratories that used their own test methods and found significantly different results for the same batch of materials. These differences arise from three main aspects:

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the test method itself, the specimen preparation and the operator's experience in compression testing. This large difference seen in compressive strengths has been and is still the source of overdesigned structures, i.e. heavier structures, which is a problem for the weight targeted application. Over the years, several test methods have been standardised. These can be divided into three groups: Shear loading [10,11], end loading [12] and combined shear and end loading methods [13]. Other non standardised tests have also been proposed such as the ICSTM test fixture [14,15]. In general, stress concentrations can arise when unsupported sections are short, while buckling may occur when the latter is too long. These can both lead to premature failures. The type of end tab (material, orientation, tapered/non tapered) and the tab-bonding technique also have a non negligible effect on the compressive strength [15,16]. Moreover, a large scatter in the strain at failure can be observed within the same batch of materials [17]. An alternative approach is to use flexural tests. These include three point bending [18], four point bending [10,19, 20], pure bending tests [17] and compression/bending tests [21–24]. We can use these tests to monitor the side of the specimen that is subjected to compression, in order to investigate the compressive behaviour of the material. For the first two, the stress concentrations found at the loading points can be critical, even though some fixtures have limited their effect [20]. However, in one version of a pure bending test, which will be used here, a compressive load is applied to a pin supported specimen of rectangular cross section. A bending moment M is induced once the Euler load is reached, thus creating a buckling instability. This test uses a simple fixture, gives reliable results and is also an interesting transition between a material and a structural test. Also, it has been observed that bending tests result in the same type of compressive failure as uniaxial compression tests, especially for thermoplastic composites [25].

The mechanisms leading to compressive failures for carbon fibre reinforced composites are governed by several parameters such as the glass transition of the material and therefore the temperature at which the test is performed [26] and many mechanical properties such as the shear modulus of the matrix [27,28] and the composite yield shear strength [28,29]. Therefore, all these properties are of interest when investigating the compressive behaviour of composite materials.

The simplicity of the pin-ended buckling test makes it suitable for the investigation of parameters such as environmental conditions (temperature and humidity). As noted previously, understanding the effect of water ingress on the compressive properties and the associated failure modes is of crucial interest. However, very few results are available in the literature [30] and even less concerning thermoplastic composite materials [31]. Water absorption in polymers is known to have significant effects on their properties. The plasticisation due to water absorption can reduce the glass transition temperature of the polymer [32,33], and swelling may introduce internal stresses. Polyamides are known to be particularly sensitive to water [34]. Water can also cause a degradation of the fibre/matrix interface [35,36].

The overall aim of the current work is to model water diffusion and its effect on the mechanical properties of thick C/PA6 composite cylinders immersed in sea water for deep sea applications (high hydrostatic pressures and low temperatures ranging from 4 to 15 °C). To provide the data for such a model, several properties are needed. Unidirectional composite materials are usually considered to be transversely isotropic. For such materials, five elastic constants are used to describe the behaviour of composite materials: the longitudinal modulus E_1, the transverse modulus E_2, the Poisson's ratio ν_{12}, the shear modulus G_{12} and the transverse shear modulus G_{23} (or the Poisson's ratio ν_{23}) [37]. Except for the latter (G_{23}), all properties were investigated here using tensile tests, as a function of homogeneous amounts of water within the laminate. Moreover, because of the targeted application, tests have also been conducted in compression (hydrostatic pressure). These data are not available in the published literature for carbon/polyamide composites. This paper will present the tests and discuss results concerning mechanical properties over a wide range of water contents.

2. Materials and methods

2.1. Materials

The main material of interest here is a C/PA6 pre-impregnated tape from Celanese® (reference: CFR-TP PA6 CF60-01). It has a fibre volume fraction of 48% and a 1-ply cured thickness of about 0.19 mm (information given by the supplier). No information is provided by the supplier related to the type of fibre or about the polymer grade. The second material, taken as a reference is a carbon-Polyetheretherketone (C/PEEK) composite supplied by Toho Tenax® (reference: -E TPUD PEEK-HTS45). The fibre volume fraction is 60% and the tape thickness is about 0.14 mm (information given by the supplier). The fibre is a HTS45 12 K carbon reinforcement from Tenax® and the PEEK matrix is a medium viscosity PEEK matrix from Evonic industries (Vestakeep® 2000). Over the past 30 years, many studies have focused on C/PEEK for structural applications (such as aircraft structures). However, using such a material for the targeted underwater applications is difficult, the latter is 10 times more expensive than the C/PA6 counterpart. Therefore, C/PA6 was chosen here as a low-cost solution.

2.2. Manufacturing process

Composite panels were manufactured by hot compression moulding. The C/PA6 panels were manufactured at 230 °C with a pressure of 5 bar. The C/PEEK panels were manufactured at 420 °C with a pressure of 10 bar. For both cycles, the cooling rate was chosen to be 20 °C/min. The manufacturing cycles are presented in Fig. 1. It should be noted that all C/PA6 plies were conditioned at 0% humidity (40 °C) until the weight stabilised to ensure that each ply was free of water before processing. Each panel that was manufactured was made of 16 plies (about 2 mm). Unidirectional $[0]_{16}$ and $[\pm 45]_{4s}$ panels were manufactured. It may be noted that the measured ply thickness after press moulding was 0.13 mm for both materials, i.e. C/PA6 and C/PEEK, which differs from the initial ply thickness.

2.3. Quality control

The quality in terms of compaction of plies of the different panels that were manufactured was checked using optical microscopy (polished sections) on a LEICA DM ILM microscope. Polished sections for C/PA6 and C/PEEK are respectively shown in Fig. 2a and b.

The void contents were determined using the software *ImageJ* from a mean of 30 images for each composite panel, according to AFNOR NF T 57-109. The degrees of crystallinity X_c were checked using DSC (Differential Scanning Calorimetry) on Q200 equipment from TA Instrument at a heating rate of 10 °C/min from the ambient temperature to 300 °C for PA6 and 400 °C for PEEK. However, the degree of crystallinity in thermoplastic composite materials is also dependent on the fibre weight fraction W_f, Eq. (1):

$$X_c = \frac{\Delta H_f}{\Delta H_f^0 \times (1 - W_f)} \times 100 \quad (1)$$

where ΔH_f is the enthalpy of fusion of the polymer and ΔH_f^0 the theoretical enthalpy of fusion for a 100% crystalline material (taken to be 188 J/g for PA6 [38], 130 J/g for PEEK [38]). After each DSC