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Moisture diffusion under hydrostatic pressure in composites

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ABSTRACT

Water diffusion under hydrostatic pressure is critical for many underwater applications. Nevertheless it has rarely been studied, and published data are contradictory. The aim of this study is to understand what governs pressure effects by studying different materials (unreinforced resin, and three glass-fibre reinforced epoxy composites). First, kinetics of water diffusion, for unreinforced resin and composite materials, are identified at different pressure levels (1, 50 and 500 bar). For the neat epoxy resin the water uptake remained unchanged when pressure was raised. The glass fibre reinforced epoxy composites produced by hand lay-up have a saturation level that increases significantly with increasing pressure, while the diffusion coefficient is unaffected. The infused composites show only a small effect of pressure slowing initial diffusion rate, while the prepreg composite show no effect. In a second part, the present study focuses on the identification of the diffusion law using a numerical method. In the final section X-ray micro-tomography is used and reveals a high level of porosity in the hand lay-up composite. Moreover, as glass fibres are hydrophobic and resin water uptake does not depend on hydrostatic pressure it is concluded that additional water diffuses into voids under pressure.

1. Background

The maximum service depth of composite use is constantly increasing in applications such as submarines, subsea oil industry structures or oceanographic profilers. Moisture diffusion in immersed composites is well known [1, 2] and its influence on mechanical properties has been studied [3–8]. However, when we consider the moisture uptake coupled with hydrostatic pressure a general trend cannot be established. While models [9, 10] tend to predict lower moisture uptake at higher pressure, experimental results can show increases [10], no effect [11], or reductions [9, 11, 12]. The aim of this work is to perform representative tests in order to understand this coupled phenomenon. Large differences in diffusion behaviour have been noted for different types of polymers. Pollard and al. in [13] established a linear relationship between pressure and moisture content in saturated glass fibre reinforced polyester.

Other studies have focused on less common matrix resins: Whitaker and al. studied in [14] the combined influence of pressure and temperature on the diffusion parameters in a polyester containing styrene monomer. In this case, pressure reduces the diffusion coefficient in the specimens only for temperatures over 25 °C, and has no influence on moisture saturation level.

Nevertheless, even for identical materials differences still exist, mainly induced by processing differences. For example, Avena and Bunsell in [11] studied the effect of hydrostatic pressure on water diffusion in two types of glass fibre-reinforced composite based on the same epoxy resin reinforced either with un-sized fibres or with fibres treated with an organosilane size. Specimens were in the form of rectangular plates (150 × 25 mm), 0.73 mm thick and with a fibre volume fraction of 60%. Tests were performed in distilled water at 23 °C under hydrostatic pressures of 1, 50, 100 and 200 bar.

Under these conditions the two materials reacted in a different way to pressure: for un-sized fibres samples, the diffusion coefficient and saturation level decreased with pressure rise whereas, for treated fibres, both diffusion parameters remained unchanged with respect to pressure variations. This clearly showed that the fibre/matrix interface can play a role in moisture ingress under pressure.

Davies et al. in [10] tested a filament wound carbon fibre-reinforced epoxy under a hydrostatic pressure of 100 bar at 60 °C for 3.5 years. Specimens were square plates (50 × 50 mm) with a thickness of 3 mm. Their study showed a significant rise in saturation level with pressure rise for specimens either dry or previously saturated without pressure (Fig. 1).

These studies illustrate the difficulty in establishing a clear, unique influence of the hydrostatic pressure on the water diffusion even for one type of material. Considering this background, the following work considers three aspects. First, the experimental procedure is described: materials used, testing conditions, measurements, and first weight gain results are presented. Then the second part is devoted to the identification of the water diffusion laws and constants for each condition. Finally parameters which influence the water diffusion under pressure are discussed.

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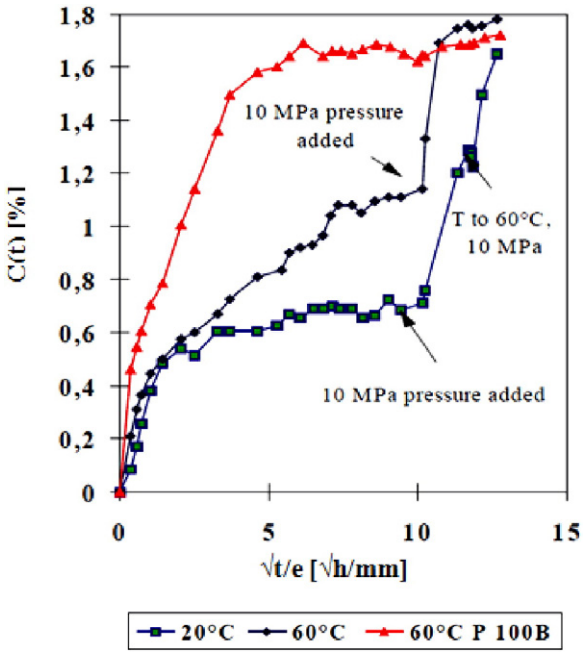

Fig. 1. Pressure influence on water diffusion in dried carbon/epoxy specimens (red) and in previously saturated specimens (blue) from [10].

Table 1
Materials tested.

Material	Thickness, mm	Vf	Tg	Porosity ratio
Epoxy resin	4.20 (± 0.20)	–	84 °C	≈0%
Hand lay-up composite	2.20 (± 0.10)	30%	80 °C	From 4% to 8%
Infused	2.25 (±0.05)	58%	75 °C	1%
Prepreg	2.20 (±0.02)	60%	110 °C	0.5%

2. Experimental

2.1. Experimental details

This study is mainly focussed on an epoxy resin and an E-glass reinforced composite with the same resin. Specimens were square plates (50 × 50 mm) with the thicknesses shown in Table 1. For both types of specimen, the resin is the commercial epoxy SR1500 (mixture of DGEBA and DGEBF) with amine hardener SD2505 (from Sicomin, France) prepared by casting plates. Samples were post-cured for 6 h at 60 °C. Table 1 summarizes the initial material properties. The volume fraction of fibres (Vf) was calculated from TGA (thermogravimetric analysis) measurements in inert gas which provide the weight fraction of resin. Glass transition temperatures (Tg) were established by a thermal technique (DSC, differential scanning calorimetry). Concerning porosity measurements, the method used is developed in section 4.

The first composite was reinforced with quasi-unidirectional glass fibres using hand lay-up, with a fibre content of 30% by volume. Two other composite materials with different epoxy resins were also tested for comparison, 2.25 mm thick infused and 2.20 mm thick pre-impregnated quasi-unidirectionally reinforced composites. The volume fractions for these were respectively 58% and 60% and the same fibre reinforcement was used for both. Fig. 2 shows micrographs of polished sections of the three composites.

Before immersion, all samples were dried at 60 °C for 15 days.

Pressure vessels (Fig. 3a and b) were manufactured to test specimens under pressures up to 1000 bar, and placed in an oven to regulate the temperature. These vessels were specially designed for rapid opening (threaded lid, see Fig. 3b), to limit measurement time. For this study, water diffusion was examined under atmospheric pressure (1 bar), low pressure (50 bar) and high pressures (250 and 500 bar) in order to highlight the effect of hydrostatic pressure. These tests on neat resin and hand lay-up composites were performed in tap water at 60 °C to increase kinetics and 5 specimens were tested in each condition. Samples were placed in racks to separate them (Fig. 3b). Reference specimens were placed in water in the same oven next to the pressure vessel. Tests on infused and prepreg materials came from a specific study in which specimens were immersed at 40 °C and 500 bars for 12 months. Again reference specimens were placed in the same oven without pressure. This second study was intended to extend the investigation to infused and prepreg glass–epoxy composites. Nevertheless these results cannot be directly compared to others performed at 60 °C.

In the case of composite materials the interfacial properties between fibres and resin can be critically affected by moisture uptake. To estimate the influence of pressure on the interfacial behaviour ILSS [15] and 4 point bending tests [16] were performed on both reference hand lay-up specimens and those subjected to pressure, after reaching saturation. Specimens tested had the following dimensions, for ILSS: 10 mm span, 15 mm × 15mm square surface, and 2.5 mm thickness, and for 4 point bending: 60 mm span, 21 mm width and 2.5 mm thickness. Both series of tests were performed on an Instron test machine with a loading speed of 5 mm/min.

Microstructural details were first examined using optical microscopy (Leica DM ILM) on polished sections, with *ImageJ* software to quantify fibre and void contents.

X-ray micro-tomography studies were then performed to analyse the microstructure of four square plate specimens in each conditions. For these studies two types of system have been used:

- The GE Phoenix V-TOM-X240 which can analyse 50 × 50mm specimens with a resolution of 28 mm^3/voxel (for beam characteristics of 100 kV and 280 mA) – Fig. 12
- MicroXCT-400 from XRadia which can analyse samples of 25 × 25mm with a resolution of 2 μm (for beam characteristics of 60 kV and 133 μA) – Fig. 15.

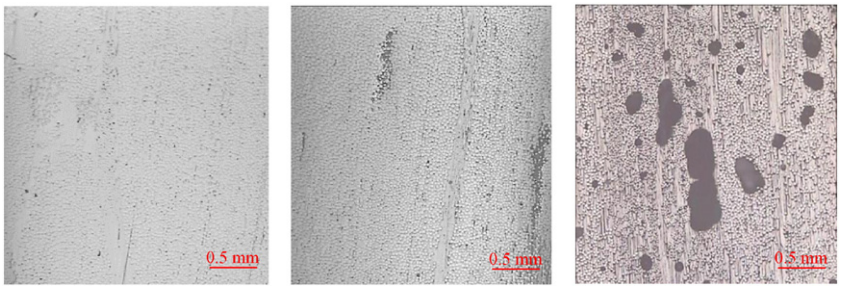

Fig. 2. Optical microscopy view of polished sections unidirectional prepreg (left), infused (centre) and hand lay-up (right) composites, sections perpendicular to fibre direction.