Stability of polyester- and vinyl ester-based composites in seawater

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Glass fiber-reinforced polymer composites are used in boats, yachts, ships, submarines and offshore drilling platforms due to their low cost, high specific strength, fatigue endurance and durability [1–6]. However, a problem with fiberglass laminates is their low Young's modulus, which makes it difficult to build ultralight marine structures with adequate stiffness. Consequently, marine composite structures requiring high stiffness are often built using carbon fiber composite. However, little published information is available on the effect of long-term seawater immersion on carbon fiber composites [4, 7]. Therefore, the aim of this research is to compare the stability of glass and carbon fiber composites in seawater. The materials studied are glass/polyester, carbon/polyester, glass/vinyl ester and carbon/vinyl ester, and these are representative of composite materials used in boats, yachts, ships, submarines and offshore drilling platforms.

The glass/polyester and glass/vinyl ester composites were reinforced with an E-glass woven fabric supplied by Fibre Glass International Pty. Ltd., Australia. The supplied glass and carbon fibers were coated with emulsion-based and epoxy-based sizing agents, respectively. The resin used in the glass/polyester and carbon/polyester composites was an isophthalic polyester resin (Synolite 0288-T-5) produced by Dulux Australia. The polyester was promoted with 2.1 parts per hundred (pph) (by weight) of 6% cobalt(II) 2-ethylhexanoate solution and catalyzed with 1.7 pph of 25% methyl ethyl ketone peroxide solution. The vinyl ester resin (Derakane 411-350) used in the glass and carbon composites was supplied by Dow Chemicals. The vinyl ester was promoted with 0.5 pph of a cobalt octanoate solution and catalyzed with 1.5 pph of 40% methyl ethyl ketone peroxide in dimethyl phthalate solution. The fiber volume fraction of the glass and carbon composites was about 65 and 57%, respectively.

All the composites were fabricated at room temperature using the wet-hand lay-up process, into flat panels measuring 120 mm by 120 mm. After fabrication, the composites were cured at room temperature for several weeks before being immersed in seawater. Some composite specimens were cured at room temperature without elevated temperature post-curing because most marine composite structures are cured under ambient conditions. The degree of resin cure was determined using differential scanning calorimetry (DSC) to be 88% for all the composites. To investigate the potential effect of this incomplete curing on the water sorption properties, some composite panels were also fully cured. Complete curing of the glass/polyester and carbon/polyester composites was achieved by heating to the material 100 °C for two hours whereas the glass/vinyl ester and carbon/vinyl ester material were completely cured by heating to 120 °C for two hours.

The composite panels were immersed in seawater with a salinity content of 2.9% and temperature of 30 ± 0.5 °C for two to four years. The panels were withdrawn from the seawater at regular intervals to monitor the weight change. The loss of chemical species from the composite specimens into the seawater was investigated to determine if there was any chemical change on the matrix. Composite panels in the under-cured and fullycured conditions were immersed in small containers containing 50 cm^3 of seawater at a temperature of 30 °C. The panels were removed after 100 days and the seawater was evaporated at room temperature to concentrate the solid residue. The organic species leached from the composite was separated from the salty residue by solvent extraction and then identified using infrared spectroscopy with a Bruker IFS88 FTIR.

Fig. 1 shows the effect of immersion time on the weight change of the glass/polyester and carbon/polyester composites in the under-cured and fully cured conditions. The immersion time was normalized to the specimen thickness to account for the minor difference in thickness between the glass/polyester and carbon/polyester panels. The profile of the water uptake curves increased rapidly with immersion time up to 3 $\text{days}^{1/2}$/mm when the weight of the composites reached a maximum value. Increasing the immersion time further caused a steady decline in the curves, and with long-term immersion the mass of the composites (except for the fully cured glass/polyester) dropped below their original weight. The weight gain

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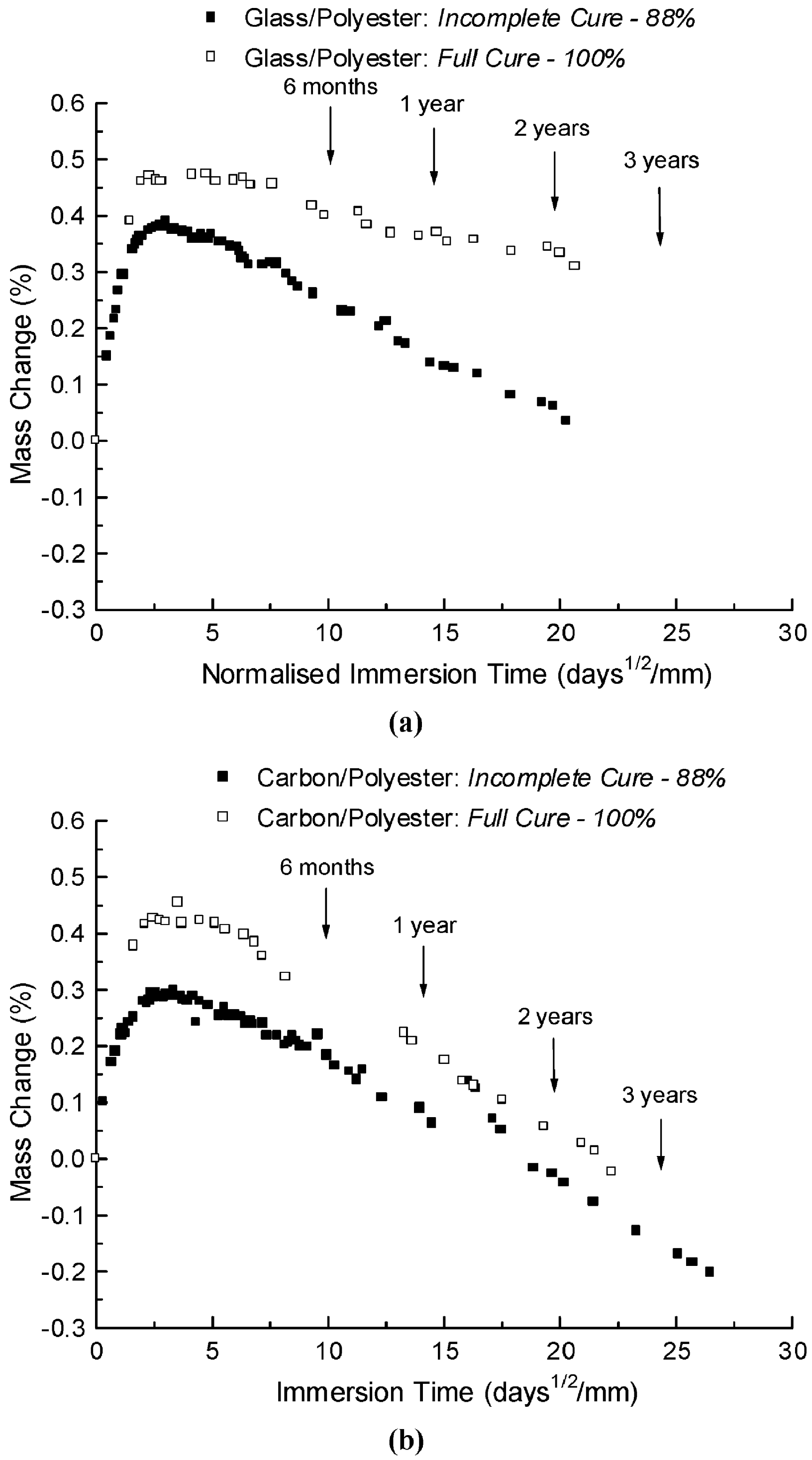
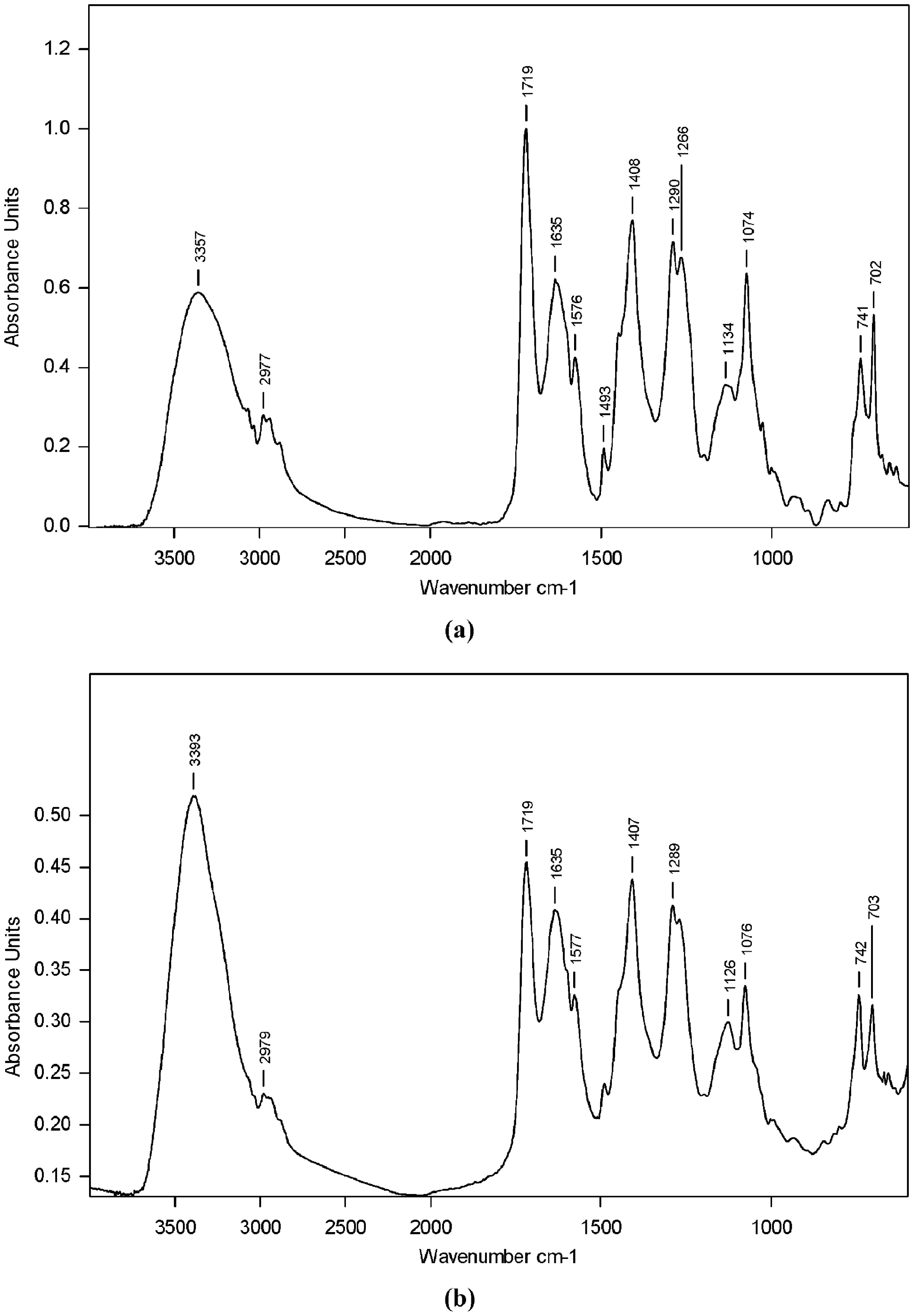


Figure 1 Water uptake curves for the (a) glass/polyester and (b) carbon/polyester composites in the under-cured and fully cured conditions.

was found to be different for the under-cured and fully cured composites, indicating that the chemical condition of the polymer matrix has a significant influence on the stability of polyester-based laminates in seawater.

The process causing the steady loss in weight of the polyester-based composites was studied by an FTIR analysis for the change in the chemical composition of the seawater surrounding the specimens. FTIR spectra of the solid residue extracted from the seawater following immersion of the glass/polyester composite in the under-cured and fully cured conditions are shown in Fig. 2. The spectra were determined after a relatively short immersion time of 100 days (or 6.7 days$^{1/2}$/mm). A variety of organic species were detected in the seawater, which were not present prior to immersion of the composite, with the concentration of the species being higher in the seawater surrounding the under-cured sample. The spectra showed peaks at 1719, 1290, 1266 and 741 cm^{-1} that indicated the presence of low-molecular weight aromatic ester species, possibly with hydroxyl end groups (hydroxyl stretching vibration at 3357 cm^{-1}). Since the ester C—O stretching vibration was at 1290–1266 cm^{-1} rather than 1235 cm^{-1} and the out-of-plane C—H from the aromatic ring adsorbs at 741 cm^{-1} rather than 730 cm^{-1},



(a)

(b)

Figure 2 FTIR spectra for the glass/polyester composite in the (a) under-cured and (b) fully cured conditions.

it was most likely an orthophthalate ester rather than an isophthalate species. This species is unlikely to originate from the resin since it is based on an isophthalate ester, unless a low concentration of orthophthalate resin was also present as it was manufactured from impure starting materials. The only other source of orthophthalate species is the dimethylphthalate carrier from the peroxide solution. Most monosubstituted aromatic compounds are likely to be present due to phenethyl alcohol that is formed by the reaction of water with styrene. Phenethyl alcohol was identified with infrared spectroscopy by purifying the salt water extracted mixture. This species would also partially account for the large hydroxyl peak (3357 cm^{-1}) in the spectra.

The infrared spectra also contained peaks at 1635 and 1408 cm^{-1} that were due to asymmetric and symmetric vibrations of ionised carboxyl groups and indicated the presence of carboxylate salt species. The carboxylate salt species probably originated from the promotor (cobalt octanoate) used to cure the polyester resin. The ester carbonyl peak at 1719 cm^{-1} shifted to a slightly lower frequency than expected, which could be due to either hydrogen bonding with hydroxyl and carboxylate salt species or the presence of carboxylic acid species. Deconvolution of the carbonyl band appeared to show a peak at 1700 cm^{-1}, and was consistent with the presence of a low concentration of carboxylic acid species. IR spectra similar to that shown in Fig. 2 was measured for the carbon/polyester composite, indicating

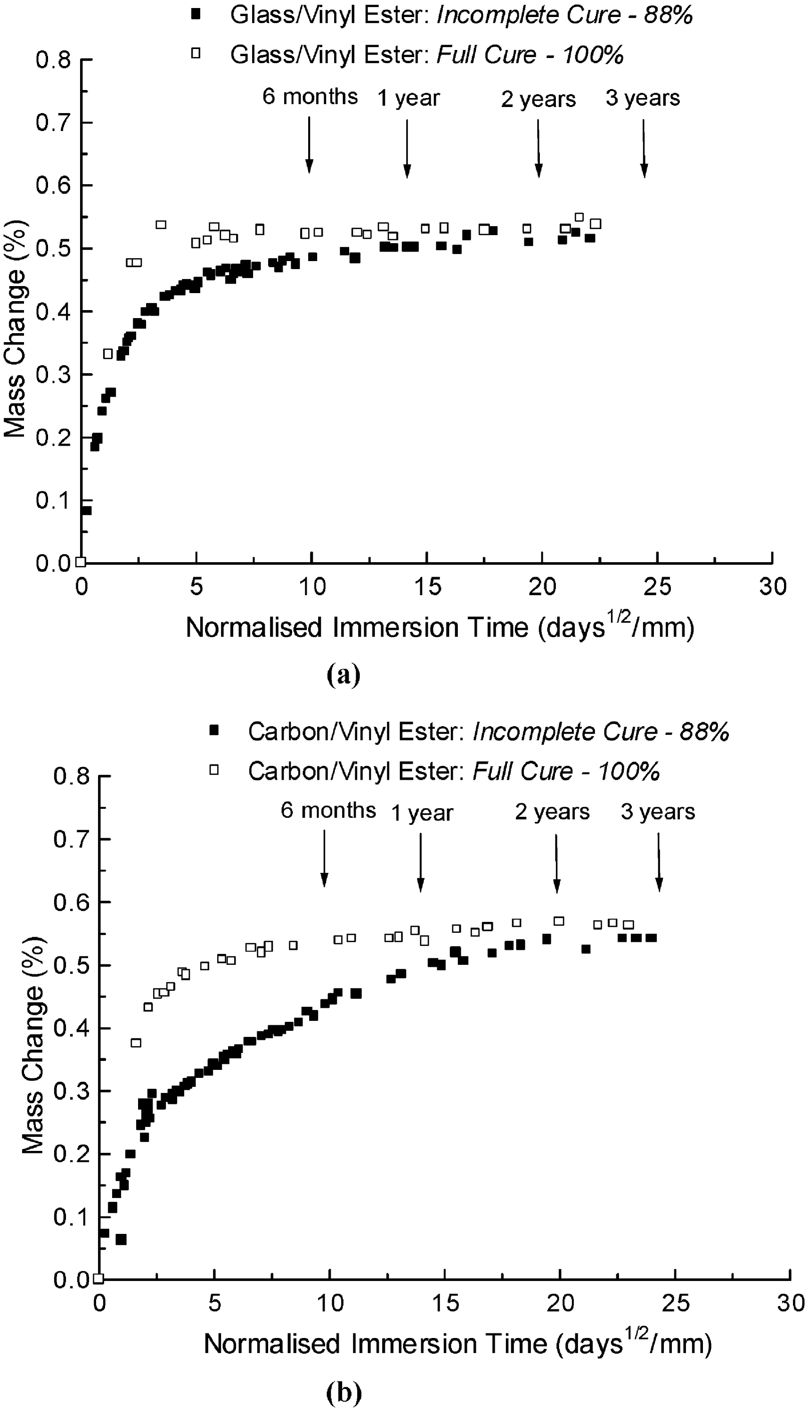
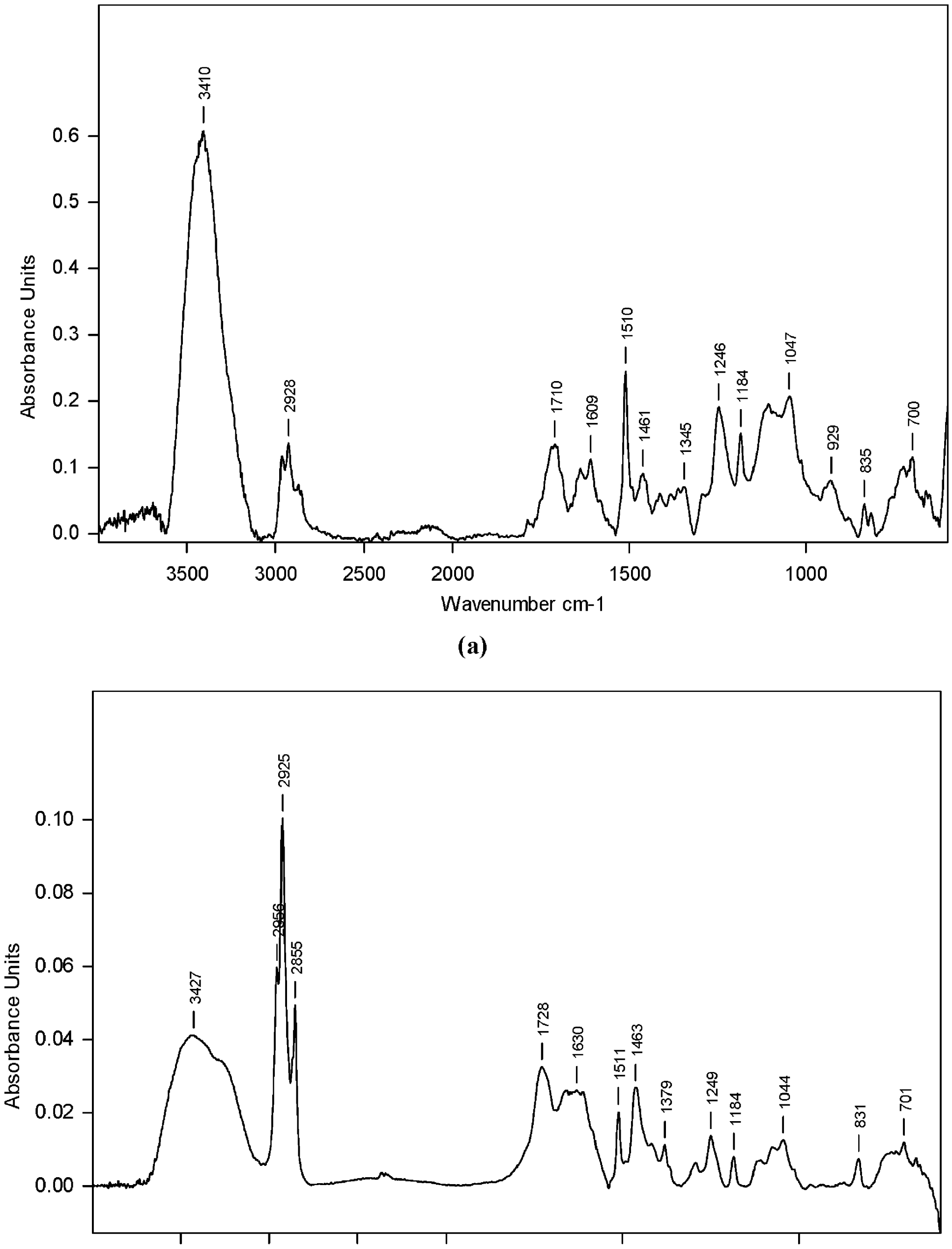


Figure 3 Water uptake curves for the (a) glass/vinyl ester and (b) carbon/vinyl ester composites in the under cured and fully cured conditions.

that this type of fiber reinforcement does not affect the process.

The effect of seawater immersion on the weight change of the vinyl ester-based composites is shown in Fig. 3. The curves show classical Fickian water uptake behavior with an initial rapid increase in weight, then reaching a plateau that is indicative of saturation. The under-cured composites gain weight more slowly, revealing that the cure condition of the vinyl ester matrix has an effect in the early stage of immersion.

FTIR spectra of the seawater residue surrounding the under-cured and post-cured glass/vinyl ester composite are presented in Fig. 4. The spectrum for the under-cured specimen is contaminated with hydrated sodium chloride (contributes to 3410 cm^{-1} hydroxyl peak) whereas the spectrum for the fully cured material contains hydrocarbon impurities (contributes to peaks at 2925, 2855 and 1463 cm^{-1}). These infrared spectra show the presence of a very low concentration of low molecular weight vinyl ester, phenethyl alcohol, and carboxylate salt species, that have been leached from the matrix. The very low levels of organic species detected indicate that the vinyl ester composites have excellent chemical stability in seawater. The FTIR spectra measured for the carbon/vinyl ester is similar to that presented in Fig. 4 for the glass/vinyl ester, indicating that the water sorption behavior is not influenced significantly by this type of fiber reinforcement.



(a)

(b)

Figure 4 FTIR spectra for the glass/vinyl ester composite in the (a) under-cured and (b) fully cured conditions.

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