The effect of matrix type on ageing of thick vinyl ester glass-fibre-reinforced laminates

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ABSTRACT

In this research, glass fibre reinforced composite laminate samples were manufactured with filament winding technique using four different vinyl ester resin systems to study ageing. The manufactured laminate samples were conditioned in an environmental cabinet (70 °C, 95 RH%), water immersion (95 °C), and in sulphuric acid solution immersion under pressure (5% H_2SO_4, 95 °C, 15 bar). After 6 and 12 months of conditioning, the samples were tensile tested and the results were compared with the initial values. Regardless of the matrix type, conditioning in the environmental cabinet resulted in the lowest weight gain and least decrease in tensile properties: the decrease in the tensile strength values was 10–25% after 12 months' conditioning depending on the vinyl ester used. The water immersion was more detrimental to the samples than the 5% H_2SO_4 immersion causing the highest weight gain and the greatest decrease in tensile strength (up to 65%). However, when comparing the tensile performance, it was noted that the highest weight gain did not inevitably correlate with the strongest ageing effect. In water immersion, the ultimate strength deteriorates faster than the proof stress level leading to a decreasing damage tolerance of the vinyl-ester composite laminates.

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1. Introduction

Fibre-reinforced plastic (FRP) composites are often the only possible economical material for the process industry in the case when the operating environment is extremely aggressive. The use of FRP composites in such applications is favoured due to their light weight combined with excellent stiffness, strength, corrosion resistance and lower price compared to highly alloyed metals. FRP materials are successfully used in marine vessels, piping, corrosion equipment, and underground storage tanks that are constantly in contact with moisture and different aqueous solutions [1,2]. These structures should have operational lifetime of several years or even decades and, therefore, their long-term properties have as much practical importance as their short-term response. During their operation, the material properties can be affected by several environmental factors, such as moisture, temperature, pressure, and chemicals. These factors may act individually or their combination may cause synergistic effects [3].

Vinyl esters are, in general, the choice of materials in applications where good corrosion resistance is required. The main body of the molecule remains unaffected when subjected to solvents due to low number of vulnerable reactive ester groups in the polymer chain [4]. The bisphenol-A based vinyl esters have two ester groups per molecule and their use in FRP structures in corrosive environments has become the industry standard. However, the incorporation of the novolac chemistry in the 1970s allowed higher service temperatures, better adhesion to fibres, and enhanced resistance to organic solvents due to higher crosslink density [4]. However, the number of ester groups in novolac based vinyl esters is higher.

The analysis of aging in the FRP materials is challenging since they are complex material systems with three distinctive components: the matrix, the fibre, and the interface region. Water molecules are very reactive since they dissolve readily giving a proton and a hydroxyl ion and can cause reversible and irreversible physical and/or chemical modifications in the FRP composite. These include plasticization and hydrolysis of the matrix, molecular degradation by polymer chain breakage, internal stresses caused by the swelling, as well as the cracking and crazing due to osmosis and the change of the water state [1]. Moisture can also diffuse into

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the fibre-matrix interface and cause debonding, leaching of fibre and reduction in fibre strength [1] as well as provide pathways for faster moisture absorption [5]. Thus FRPs are typically more prone to the detrimental effects of water compared to the bulk polymer of the same resin. The absorbed moisture generally decreases the glass transition temperature T_g of the composite, and softens the material causing a loss in the stiffness and strength, especially at elevated temperatures. In vinyl esters, the water uptake causes plasticization over a short-term conditioning and hydrolysis over a long term conditioning through the breakage of the ester linkages [6].

The long-term mechanical performance of different FRP materials has been extensively investigated. Vinyl ester based FRP [7–12] has gained significant interest in research, yet polyester [13–17,18] based materials have also been studied. Generally, a decrease in tensile [9,10,13,18], flexural [9–11,15,16,18], shear [8,11,17], and impact [11] properties is observable after environmental conditioning. For example, Cabral-Fonseca et al. [10] have measured up to 40% decrease in the tensile strength values of pultruded vinyl ester profiles after a long-term water immersion at elevated temperatures. The decrease was more pronounced as the conditioning temperature was increased. In addition to temperature, the immersion medium has a significant effect on the long-term properties. Demineralized water, for example, has shown to have more aggressive effect compared to salt water due to osmotic effects [10].

The changing of the neutral ageing environment into an acidic or alkaline environment has shown to have varied effects: Hammami et al. [11] have noticed a clear decrease in the flexural properties of glass fibre reinforced vinyl ester composites when exposed to nitric acid solution. In that case, the decrease in properties was more pronounced as the concentration was increased from 2% to 5% or when the immersion time was extended. In a seawater immersion, the resulting decrease in stiffness was less than for nitric acid solution. When considering sulphuric acid media, it has been concluded that a polymer matrix cannot be regarded as a good barrier against water but it resists well the penetration of SO_4^{2-} ions [19]. Therefore, pure water immersion may be more detrimental to the FRP materials than dilute acid solutions. In fact, in our earlier study, water immersion was shown to have stronger effect on the FRP composite during a three-day test in 95 °C than a 5% H_2SO_4 solution: The samples tested in water showed significantly higher weight gain and increased erosion wear rate [20]. Similarly, Agarwal et al. [13] have measured a tensile strength decrease of 20% after water immersion, while the decrease was only 10% after 10% H_2SO_4 solution conditioning. However, a direct relation between the decrease in tensile strength and the solution concentration could not be drawn.

In this study, the performance of FRP materials is examined after a long-term conditioning. Four different commercial vinyl ester resins were used and the composite samples were exposed to one of three different environmental conditions: environmental cabinet (relative humidity 95% and temperature 70 °C), water immersion (temperature 95 °C), and pressurized 5% H_2SO_4 solution immersion (temperature 95 °C and pressure 15 bar). The weight gain and the changes in the glass transition temperature (T_g) values of the composites were monitored along with the tensile response of the composites.

2. Experimental details

2.1. Materials

In this study, four different vinyl ester resins were used as the matrix material in the composites: Derakane 441-400 (supplied by Momentum), Atlac E-Nova FW 1045 (supplied by DSM), Dion 9400 (supplied by Reichhold), and Derakane 455-400 (supplied by Momentum). The main goal of this study was to evaluate how the innate resin properties correlate with the long-term properties of the composite laminates. This study includes both bisphenol-A based vinyl esters (Derakane 441 and Atlac E-Nova FW 1045) and novolac based vinyl esters (Dion 9400 and Derakane 455). In addition, Atlac E-Nova is a flexibilized bisphenol-A based vinyl ester urethane resin. Vinyl ester urethane modified resins generally show higher T_g than that of corresponding unmodified, solely styrene crosslinked resins [21].

The main properties of the applied resins are presented in Table 1. Based on the resin suppliers' data, the heat distortion temperature (HDT) is clearly lower in the bisphenol-A based resins than in the novolac based resins. However, all the resins should tolerate high service temperatures (up to 95 °C) without a significant deterioration.

In the vessels for aggressive chemicals, the FRP wall typically contains two distinctive layers: a structural layer, which has the main function in providing load bearing capacity for the structure, and a resin rich corrosion barrier layer (resin content roughly 75%), which protects the structural layer from chemical attack [26]. In this study, glass fibre reinforced vinyl ester pipe samples (Fig. 1a) were manufactured using a filament winding technique. All the pipe samples had a lay-up with structural and corrosive layers (Fig. 1b–c). The structural layers contained 20 layers of woven roving (3B-fiberglass R25HX14, 480 g/m^2) and 16 layers of axial roving (Ahlstrom 9690-19-300, 256 g/m^2). The axial roving was applied parallel to the symmetry axis of the pipe one after another with the woven roving. The total thickness of the structural layer was roughly 13 mm. A thick corrosion layer was manufactured on the other side of the samples using nine layers of chopped strand mat (Owens Corning M723A, 300 g/m^2) and one layer of ECR-glass surface mat (Owens Corning M524-ECR30S, 30 g/m^2) on the top. The total thickness of the corrosion layer was roughly 7 mm. The darker, resin-rich corrosion layer was placed on the inner or outer side of the sample (Fig. 1b–c). The nominal overall thickness of the pipe wall was 20 mm. All the pipe samples were post-cured according to the resin suppliers' instructions: FRP-441 for 10 h at 80 °C, FRP-Atlac 5 h at 90 °C, FRP-Dion 8 h at 80 °C, and FRP-455 10 h at 100 °C. For conditioning, the filament-wound pipe was cut in laminate segments of 400 × 400 mm^2.

2.2. Exposure conditions

In this study, three conditions were used to investigate the ageing of the laminates: a humid condition, a water immersion and an acidic immersion. While the hot acidic immersion is close to the actual industrial environment, the change between the water and acidic immersion reveals the effect of the acid and the change between the water immersion and the humid condition the effect of high mass uptake. The laminate segments were exposed to one of the three different environmental conditions for a maximum of 12 months. The segment properties were tested after 6 and 12 months of conditioning. Prior to conditioning, the laminate edges were sealed with a gelcoat (supplied by Ashland) to prevent excess water absorption via the free cut surfaces. The humidity conditioning was conducted by Weiss SB22 environmental chamber at a temperature of 70 °C and relative humidity of 95%. The water immersion was conducted by a water bath at a temperature of 95 °C. For the acidic conditions, a pressurized reactor was filled with 5% H_2SO_4 solution. Also 0.5 g/l of $Fe_2(SO_4)_3$ was added to act as a corrosion inhibitor for the metallic parts of the reactor. A total of four pressurized reactors were used, so that the segment samples manufactured with a specific resin were conditioned in individual reactors, separated from the other segment samples. The temperature of the solution was 95 °C and the pressure inside