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The influence of high-temperature sulfuric acid solution ageing on the properties of laminated vinyl-ester joints

M. Lindgren ^{a,*}, M. Wallin ^b, M. Kakkonen ^c, O. Saarela ^b, J. Vuorinen ^c

^a Outotec Research Center, P.O. Box 69, 28101 Pori, Finland

^b Department of Mechanical Engineering, Aalto University, P.O. Box 14300, FI-00076 Aalto, Finland

^c Department of Materials Science, Tampere University of Technology, P.O. Box 589, 33101 Tampere, Finland

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ABSTRACT

A carbon fiber powder doped corrosion layer is used as an inner layer in large composite tanks to improve their chemical and wear resistance. In joints fabricated on site, this layer is embedded into the structure. This study evaluates the lap shear strength of specimens, simulating a laminated joint in between the corrosion layer and the inner joint laminate. Lap-shear tests were carried out for as-fabricated and aged laminates at room temperature and at elevated temperature. Ageing was carried out for half a year in a 95 °C pressurized sulfuric acid solution. The tests showed that, after ageing, the room temperature shear strength remained unaltered but high-temperature shear strength was lowered. When the temperature increased, the failure location shifted from the interface between the doped layer and the joint laminate to the doped layer. Thermal analysis and microscopy were employed to clarify the reasons for the observed behavior.

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1. Introduction

Fiberglass reinforced plastic composites (FRP) are often used to construct tanks, piping, scrubbers, launders and other components for use in corrosive environments, e.g. in the mining and metallurgical industry [1]. FRP typically offers superior and cost effective corrosion resistance relative to other construction materials. It comprises three different distinct phases (fibers, matrix, and fiber–matrix interfacial layers). These phases are affected in different ways when water or some aggressive chemical enters the material from the environment.

The glass fibers that give structural stiffness and strength for FRP laminates are practically insensitive to moisture but various acids have an adverse effect on the strength properties of normal E glass fibers [2,3]. Additionally, E glass is prone to stress-corrosion cracking [4–6]. ECR glass has been shown to degrade to a far lesser extent under acidic conditions [5–7]. Consequently, ECR glass fibers are applied in corrosive environments either throughout the structure or within the resin-rich corrosion layer, protecting the underlying structural layer.

The polymeric matrix is sensitive to moisture, in addition to potentially aggressive chemicals, because water interacts with

* Corresponding author. Tel.: +358 40 829 7293; fax: +358 20 329 3201

E-mail addresses: mari.lindgren@outotec.com (M. Lindgren), markus.wallin@aalto.fi (M. Wallin), markus.kakkonen@tut.fi (M. Kakkonen), olli.saarela@aalto.fi (O. Saarela), jyrki.vuorinen@tut.fi (J. Vuorinen).

polymers physically, i.e. plasticization, and/or chemically, i.e. hydrolysis. Water is chemically very reactive because it has a polar molecule H–OH, which dissociates readily giving a proton and a hydroxyl ion. A polymeric network contains numerous reactive sites and is held together by hydrogen bonds and other secondary valence forces between the adjacent polymer chains. For example, through hydrogen bonding, water molecules bind to epoxy resins, forming type I and type II bound water, depending on the bond strength [8]. Rupture of the interchain bonds allows the polymer network to expand and, as a result, bound water induces swelling [9]. In addition to bound water, there is some free volume in the polymer (including voids). Obviously, water can occupy these free volumes and it is then labeled free water. Compared to polyester, vinyl ester is more resistant to degradation since it has fewer ester groups, which are weak points for hydrolysis [13]. Consequently, vinyl ester is favored in corrosive conditions.

The stability of the fiber–matrix interfacial layer governs the mechanical properties of a fiber-reinforced composite, especially under hot and wet conditions [10]. Glass fibers are highly hygroscopic. Therefore, water accumulates at unprotected glass fiber surfaces over periods of time causing a loss of adhesion. A study of glass-reinforced isophthalic polyester by the nuclear magnetic resonance technique has demonstrated the tendency of water to concentrate at the fiber–matrix interface; the concentration of water there was found to be twice that of the bulk of the matrix [11]. Strong chemical interaction between the fibers and the matrix, e.g. through silane coating [11,12], prevents moisture

penetration at the interface promoting the retention of mechanical properties.

Moisture penetrates a laminate mainly through direct diffusion of water molecules into the matrix. The other mechanisms that may become active are capillary flow along the fiber–matrix interface and transport through microcracks. At low temperatures, moisture absorption is often found to follow Fickian-type diffusion [15]. At higher temperatures, the complementary diffusion paths, through micropores for example, gain importance and more complex behavior has been observed [16–18]. A mechanically damaged laminate has been found to absorb water more quickly and the saturation moisture content has been higher compared to its undamaged counterpart [19].

The exposure of a laminate to a hot and wet environment or to certain chemical environments leads to a noticeable deterioration of mechanical properties, such as tensile strength [21–23], elastic modulus [22], and interlaminar shear strength [12,24], influencing the integrity of the structures. In addition, changes in physical properties that manifest themselves as, for instance, a lowering of the glass transition temperature have typically been reported [20]. The samples, however, have often comprised E glass fibers and no corrosion barrier has been used. Both features differ from the laminates aimed for aggressive chemical environments. Consequently, the reported deterioration rates may be overestimated when applied to laminates designed for corrosion service.

In large tanks in the mining and metallurgical industry, joints between substructures, such as the cylinder shell and the bottom, are partly made in the workshop and partly on site. The joint between the bottom and the cylinder shell can be critical [25]. In this type of joint, the primary load-carrying member is normally the outer joint laminate and the main function of the inner joint laminate is to seal the joint. Nevertheless, the inner joint inevitably bears a certain amount of the load but its long-term properties after ageing are not known. In this experimental study, a laminate representing an inner joint added on top of a carbon fiber powder doped corrosion layer was manufactured and aged in a sulfuric acid solution and its properties were characterized.

2. Materials and methods

Several similar test laminate samples were prepared and half of them were aged for half a year in a high-temperature sulfuric acid solution. Lap shear tests were carried out for the as-fabricated and aged laminate samples at room temperature and at elevated temperature. Thermal analysis was also conducted for the as-fabricated and aged samples and selected fracture surfaces were characterized with a scanning electron microscope. Table 1 summarizes the experimental investigations.

2.1. Test laminate

The test laminate was prepared from Derakane 441-400 vinyl ester resin and ECR glass fibers using a glass plate as a mold. According to the datasheet of the resin [26] glass transition temperature T_g of the resin is 125 °C, tensile strength 90 MPa and

tensile elongation at yield 5%–6%. The first part of the laminate consisted of a 3 mm thick corrosion barrier layer that was laid onto the mold surface, and a 7 mm thick structural layer that was added on top of the corrosion layer. Together the layers represented the inner portion of a tank bottom laminate that is typically joined on site. The corrosion layer consisted of one surface mat of ECR glass and eight layers of Advantex chopped strand mat (Owens Corning M723A 300 g/m²). The resin of the corrosion layer was doped with carbon fiber powder (CFM-PYR-H1; pyrolysis recycled HTS-type carbon fibers, medium fiber length 200 μm, concentration 5% by weight.). As a result of the doping, the corrosion layer was black in color. The laminate, later referred to as the *base laminate*, was cured for 4 h at 80 °C and 1 h at 100 °C.

After curing, the doped surface of the base laminate was sandblasted and the *joint laminate* was prepared on top of the surface in two phases. First, an infused laminate consisting of two mat layers (powder bound chopped strand mat 450 g/m²), four fabric/mat layers (Ahlstrom 5520/M100-125-40, 1374 g/m²), and one mat layer (450 g/m²) was added. Secondly, a hand laminate consisting of similar reinforcements was applied. The curing and post-curing of the joint laminate was similar to the curing of the base laminate, i.e. 4 h at 80 °C and 1 h at 100 °C.

The glass fractions of the laminates were measured with a residual ash determination test where a small sample (weight approximately 1 g) was cut from the laminate and its temperature was raised gradually to 600 °C in an oven. After all the resin had burned away the remaining ash was weighed and compared to the original weight. The glass volume content of the base laminate was determined to be 27 ± 1 wt% in the corrosion layer and 42 ± 1 wt% in the structural layer. The glass volume content of the joint laminate was on average 46 ± 1 wt%, although some differences between the hand laminate and infused laminate were found. The carbon fiber doped layer contained the largest pores. In fact, all the visually observable pores were seen in that layer. The joint laminate adjacent to the carbon doped layer contained numerous smaller pores, as illustrated in Fig. 1.

Half of the test laminate was aged in four separate pieces. Before ageing, the edges of the laminates were sealed with vinyl ester resin. The laminates were weighed before and after immersion. The laminates were aged for half a year completely immersed in a 50 g/l sulfuric acid solution (about 5% H₂SO₄), containing 0.5 g/l ferric sulfate. Ferric sulfate was added to act as a corrosion inhibitor for the stainless steel parts of the set-up. The nominal temperature of the solution was 95 °C and the nominal pressure 15 bar. The temperature and pressure were monitored continuously. The measured temperature varied between 93 and 95 °C and the measured pressure between 13 and 15 bar. The H₂SO₄ concentration was measured by titration before and after the experiment and was found to remain unchanged. The iron concentration was measured by inductively couple plasma (ICP) and was found to increase somewhat due to corrosion of the stainless steel parts.

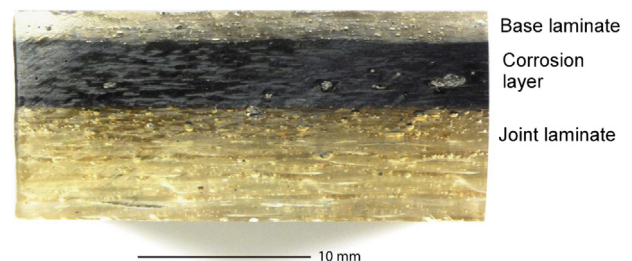


Fig. 1. Optical micrograph of the test laminate around the carbon fiber powder doped (black) layer.

Table 1
Summary of the experimental investigations.

Laminate	Room temperature (RT) lap shear tests	Elevated temperature lap shear tests	Thermal analysis	Fracture surface examination
As-fabricated	X	105 °C	X	RT, 105 °C
Aged	X	80 °C, 95 °C and 110 °C	X	RT, 80 °C, 95 °C and 110 °C

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