Polymer Degradation and Stability 98 (2013) 853–862

Contents lists available at SciVerse ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Effects of alkaline and acid solutions on glass/epoxy composites

A.M. Amaro [a,*], P.N.B. Reis [b], M.A. Neto [a], C. Louro [a]

[a] CEMUC, Department of Mechanical Engineering, University of Coimbra, Rua Luís Reis Santos, Pinhal de Marrocos, 3030-788 Coimbra, Portugal
[b] Department of Electromechanical Engineering, University of Beira Interior, Covilhã, Portugal

ARTICLE INFO

Article history:
Received 26 June 2012
Received in revised form
24 October 2012
Accepted 27 December 2012
Available online 11 January 2013

Keywords:
Composites
Environmental degradation
Failure
Hardness measurement
Mechanical characterization

ABSTRACT

Composite structures can be exposed to a range of corrosive environments during their in-service life, which causes degradation in terms of material properties. The effect of alkaline and acid solutions on the GRP mechanical properties can be found in open literature, but the studies presented are not sufficient to establish a full knowledge of this subject. In this paper the flexural properties and the impact strength of a glass fibre/epoxy composite after immersion in hydrochloric acid (HCl) and sodium hydroxide (NaOH) were analysed. Independently of the solution, the flexural strength and the flexural modulus decrease with the exposure time. However, alkaline solution promotes higher decrease of the flexural properties than the acid solution. The same tendency was observed for impact strength.

1. Introduction

The interest in glass-reinforced plastics (GRP) components for highly corrosive environments, as an alternative to stainless or coated steel ones, is becoming common. They offer an attractive potential for reducing the weight, as consequence of their high specific strength and stiffness, competitive cost, good static and dynamic properties, good resistance to corrosion and simplified fabrication.

Nowadays, composite pipes are largely used in the chemical industry, building and infrastructures [1]. On the other hand the use of the GRP tanks in hydrometallurgical process plants or other components is becoming common [2]. However, GRP tanks and pipes may be degraded due to abrasion, change in brittleness or hardness, delamination or separation of fibre from matrix and degradation of matrix due to high speed flow of hard particles, cyclic loading and unloading of tanks, diffusion of acid solutions and so on [2].

The effect of alkaline and acid solutions on the GRP mechanical properties can be found in open literature, but the studies presented are not sufficient to establish a full knowledge of this subject. Mahmoud et al. [3] shows that the change in the flexural strength, hardness and Charpy impact resistance depends upon the type of acids and the period of immersion. For example, relatively to HCl, flexural strength was found to be insensitive until 30 days of immersion and, after this period, a decrease can be observed around 10%. In terms of hardness, they showed that the Barcol hardness of the polyester drops around 15% after 90 days of exposure. However, for external pipe surface the hardness was found to be insensitive until 30 days of immersion, while for internal surface this phenomenon was verified until 60 days. In terms of Charpy impact resistance a slight decrease, around 5%, can be observed until 60 days of immersion and in last 30 days (between 60 and 90 days) a significant drop of 10% occurs. Combining the HCl effect with temperature, all properties above mentioned decreased significantly. Polyester and bisphenol A epoxy vinyl ester resins were exposed to two different acidic solutions (1M H2SO4, Co spent electrolyte), at two different temperatures (25 °C, 75 °C) and for two exposure durations (1 week, 4 weeks) by Banna et al. [2]. They concluded that the polyester resin had lower modulus values when exposed to higher temperature solutions or higher exposure duration compared to the bisphenol A epoxy vinyl ester resin. For both resins the average hardness increased after 2 weeks of exposition and then decreased after 4 weeks exposure (but still higher than the unexposed). Finally, the microstructure of the polyester degraded more under acid and higher temperature exposure as indicated by increased surface roughness, cracks and diffusion of sulphur into the cracks. On the other hand, Stamenovic et al. [1] studied the effect of alkaline and acid solutions on the tensile properties of

* Corresponding author. Tel.: +351 239790700; fax: +351 239790701.
E-mail addresses: ana.amaro@dem.uc.pt (A.M. Amaro), preis@ubi.pt (P.N.B. Reis), augusta.neto@dem.uc.pt (M.A. Neto), cristina.louro@dem.uc.pt (C. Louro).

0141-3910/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymdegradstab.2012.12.029

glass-polyester composites. They concluded that the alkaline solution decreases the tensile properties (ultimate tensile strength and modulus) and this tendency increases with the pH value. Concerning the acid solutions, they increase the tensile properties and this tendency was more relevant when the pH value decreases. For both solutions, Stamenovic et al. [1] concluded that the changes observed on the tensile properties are proportional with the exposure time (number of days in liquid). The effects of sulphuric acid concentration and the sequential layup of glass fibre reinforcements on the diffusion behaviour glass/epoxy laminates were studied by Pai et al. [4]. The results showed that composite specimens with chopped strand mat as the skins layers exhibited higher weight gain than those with woven roving mat as the skin layers. Material degradation is more pronounced with the increase of sulphuric acid concentration, which can be explained by hydrolytic dissolving of the matrix in contact with this acid [1, 4]. Degradation studies were carried out in different solvents like 10% NaOH, 1 N HCl and 10% NaCl by Sindhu et al. [5] and its influence on mechanical properties was analysed. It was observed that the tensile strength and the modulus (E) increases in acid environments and decreases for the other solvents. Finally, several studies were performed on GRP under stress corrosion cracking conditions [6–11]. According to Kawada and Srivastava [11] stress corrosion cracking in GRP occurs as a result of a combination of loads and exposure to a corrosive environment. Sharp cracks initiate and propagate through the material as a direct consequence of the weakening of the glass fibres by the acid. The strength of the fibre reduces dramatically as a result of diffusion of acid and chemical attack of the fibre surface at the crack tip, which causes a highly planar fracture with a much reduced failure stress.

The aim of this work is study the flexural and low velocity impact response of a glass fibre/epoxy composite after immersion in hydrochloric acid (HCl) and sodium hydroxide (NaOH). Intends to increase the knowledge of the material degradation by two different solutions, an acid and an alkaline solution, in terms of flexural and impact strength. The bending test was selected because, according to Banna et al. [2], is the most sensitive to the change of exposure conditions. On the other hand, impact damage is considered the primary cause of in-service delamination in composites, which are very dangerous because they have severe effects on the performance of those materials [12–17]. This subject, low velocity impact associated with highly corrosive environments, is not reported in bibliography yet and the low velocity impact is the most serious problem, given the difficulty of its visual detection [18,19].

2. Material and experimental procedure

Composite laminates were prepared in the laboratory from glass fibre Prepreg TEXIPREG® ET443 (EE190 ET443 Glass Fabric PREPREG from SEAL, Legnano, Italy) and processed in agreement with the manufacturer recommendations, using the autoclave/vacuum-bag moulding process. The laminates were manufactured with the stacking sequence $[45_2, 90_2, -45_2, 0_2]_s$. The processing setup consisted of several steps: make the hermetic bag and apply 0.05 MPa vacuum; heat up to 125 °C at a 3–5 °C/min rate; apply a pressure of 0.5 MPa when a temperature of 120–125 °C is reached; maintaining pressure and temperature for 60 min; cool down to room temperature maintaining pressure and finally get the part out from the mould. The plates were manufactured in a useful size of $300 \times 300 \times 2.1$ mm^3.

The specimens used in the experiments were cut from these thin plates, using a diamond saw and a moving speed chosen to reduce the heat in the specimen. The static three point bending tests were performed using specimens cut nominally to $100 \times 14 \times 2.1$ mm^3. On the other hand, the samples used in the impact tests were cut from those thin plates to square specimens with 100 mm side and 2.1 mm thickness ($100 \times 100 \times 2.1$ mm^3). Before corrosive exposure the impact samples were subjected to an impact of 8 J, by an impactor with diameter of 10 mm and mass of 3.4 kg.

The specimens were completely submerged into hydrochloric acid (HCl) and sodium hydroxide (NaOH). Both solutions presented a concentration of 10% in weight (wt.%) and the pH level is 13.0 and 1.5, respectively, for NaOH and HCl [20]. The exposure temperature was 25 °C (room temperature) and the exposure durations were 12, 24 and 36 days. It is important to note that the both faces of composites were exposed to acid and alkaline environments, however, in real conditions only one face of composite structures is exposed. Afterwards, they were washed with clean water and dried at room temperature.

The bending tests were performed according to ASTM D790-2, using a Shimadzu AG-10 universal testing machine equipped with a 5 kN load cell and TRAPEZIUM software at a displacement rate of 5 mm/min. All 3PB tests were also carried out at room temperature, with a span of 34 mm and, for each condition, 5 specimens were used.

Bending strength was calculated as the nominal stress at middle span section obtained using maximum value of the load. The nominal bending stress was calculated using:

$$\sigma = \frac{3PL}{2bh^2} \tag{1}$$

being P the load, L the span length, b the width and h the thickness of the specimen. The stiffness modulus was calculated by the linear elastic bending beams theory relationship

$$E = \frac{\Delta P \cdot L^3}{48 \Delta u \cdot I} \tag{2}$$

where I is the moment of inertia of the cross-section and ΔP and Δu are, respectively, the load range and flexural displacement range at middle span for an interval in the linear region of the load versus displacement plot. The stiffness modulus was obtained by linear regression of the load–displacement curves considering the interval in the linear segment with a correlation factor greater than 95%.

The low velocity impact tests were made using a drop weight-testing machine Instron-Ceast 9340. An impactor with a diameter of 10 mm and mass of 3.4 kg was used. The tests were performed on circular section samples of 70 mm and the impactor stroke at the centre of the samples obtained by centrally supporting the 100×100 mm specimens. The impact energy used for the first impact was 8 J, which corresponds to an impact velocity of 2.16 ms^{-1}. All the other multi-impacts were performed using impact energy of 4 J, which corresponds to an impact velocity of 1.53 ms^{-1}. For each condition, five specimens were tested at room temperature. After impact tests, all the specimens were inspected in order to evaluate the size and shape of the delaminations. As the glass-laminated plates are translucent it is possible to obtain the image of the damage using photography. To achieve the best possible definition of the damaged area, the plates were photographed in counter-light using a powerful light source. Plates were framed in a window so that all the light could fall upon them.

In order to obtain the solvents absorption it was used the following procedure, in accordance with BS EN ISO 62:1999. The samples were placed in an oven at 40 °C for 6 h, then cooled and weighed in order to obtain the dry weight (DW). Afterwards, a series of samples were immersed in the respective solutions (HCl and NaOH) and periodically weighted to obtain the current wet weight (CWW). The water absorption in weight percentage (W%) was calculated from Eq. (3):