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Hygrothermal ageing of adhesive joints with nanoreinforced adhesives and different surface treatments of carbon fibre/epoxy substrates

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ABSTRACT

The effect of water absorption on the strength of single lap adhesive joints subjected to accelerated hygrothermal ageing (55 °C, 95% relative humidity, 800 h) was analysed. Two different variables were studied: the surface treatment of the carbon fibre/epoxy laminates (peel ply, grit blasting and atmospheric pressure plasma) and the addition of carbon nanofillers (0.5 wt% nanofibres and 0.25 wt% nanotubes) to the epoxy adhesive. The joint strength and the failure mode of the joints were investigated. Furthermore, the amount of water absorbed by the adhesive was determined.

Adhesive joints with peel ply-treated laminates exhibit an increase in their strength, which is attributed to a relaxation of stresses in the adhesive/laminate interface; with grit blasting, this property remains almost constant. Plasma treatment provides the worst ageing behaviour because this treatment results in a surface with a higher surface free energy, which is more susceptible to environmental attack. The nanoreinforcement of the adhesive has a beneficial effect: it decreases the amount of absorbed water.

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1. Introduction

The environmental durability of adhesive joints in different aggressive media is an important characteristic that should be considered when designing composite structures. In an aircraft, for example, carbon fibre/epoxy structures might be subjected to several fluids, such as paint strippers that contain dichloromethane, aviation fuel, deicing fluids that contain propyleneglycol, hydraulic fluids or water [1].

Epoxy adhesives are one of most used adhesives for joining composite materials. These adhesives are usually modified with thermoplastic or elastomeric polymers to increase their toughness and impact strength. However, these additives might decrease the elastic modulus and the glass transition temperature [2,3]. In recent years, a novel trend has been the addition of small amounts of carbon nanofillers with the goal of improving the thermal, mechanical and electrical behaviour of epoxy resins and adhesives [4–9]. An increase of the electrical conductivity to levels that are sufficiently high to allow the dissipation of electrostatic charges has already been achieved [10]. However, the effect of carbon nanofibres and carbon nanotubes on the glass transition temperature of epoxy resins is not clear [4,6,11–13],

and the obtained mechanical properties are not as good as expected because of the agglomeration and entanglement of these nanofillers [14,15].

Despite the considerable number of studies on the addition of carbon nanotubes or nanofibres to epoxy resins, there is little information about their effect on water absorption and the loss of properties after environmental ageing or water immersion. Only a few researchers have worked on this topic. Jana and Zhong studied the moisture absorption of epoxy resin with different contents of graphitic nanofibres, and they observed that these composites exhibit behaviour similar to pure epoxy [16]. Regarding the adhesive joints, Yu et al. analysed the effect of adding carbon nanotubes to an epoxy adhesive on the durability of aluminium bonds [17]. They demonstrated that the presence of carbon nanotubes improves the behaviour of these joints after immersion in water, decreases the initial crack length and slows the crack propagation during wedge tests.

In this work, we have studied the effect of hygrothermal ageing at 55 °C and 95% relative humidity (RH) for 800 h on the lap shear strength of adhesive joints in carbon fibre/epoxy laminates. The effect of the surface treatment of these substrates and the reinforcement of the epoxy adhesive with carbon nanofillers were evaluated to compare the influence of these parameters on the ageing behaviour of adhesive joints.

The surface treatments applied to the laminates were peel ply, grit blasting and atmospheric pressure plasma. Peel ply is a commonly used surface treatment in the aerospace industry.

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A polyester ply was chosen because it does not require a releasing agent to be removed, unlike the nylon peel ply. Both plies protect the laminate from external contaminants; however, because nylon plies require the use of a releasing agent, these plies internally contaminate the surfaces themselves [18]. Grit blasting is a very simple and cheap surface treatment. The primary drawback of this technique is that it may damage the carbon fibres of the laminates [19,20]. Plasma treatment provides better results than peel ply and grit blasting in terms of surface energy and joint strength [20,21]. Furthermore, atmospheric pressure plasmas present in-line processing capabilities, are less expensive and provide better results than low-pressure plasmas [22,23].

During the environmental ageing of adhesive joints, water may enter through the adhesive, the substrate or the adhesive/substrate interface, and it is capable of affecting the properties of each of these elements. Therefore, the fractographic study of the tested joints will be very helpful for establishing their failure mode and explaining the obtained results.

2. Experimental

2.1. Materials

The adhesive used is based on the diglycidyl ether of bisphenol A (DGEBA), with a 178 g/epoxy equivalent, and it was cured with 4,4′-diaminodiphenylmethane (DDM), with a 49.6 g/amine equivalent. Two types of carbon nanofillers were added to this adhesive: carbon nanofibres (CNFs) and carbon nanotubes (CNTs). The carbon nanofibres were manufactured using the catalytic carbon vapour deposition (CCVD) method by Grupo Antolin (GANF-1). The diameter of the CNF depends on their structure, and it ranges from 12 to 100 nm; according to the manufacturer, their length is longer than 30 μm [24]. Amino-functionalised multiwalled carbon nanotubes (Nanocyl-3152), which were also manufactured using the CCVD method, had an average diameter of 9.5 nm and an average length that was less than 1 μm. As specified in the datasheet [25], the extent of functionalisation is less than 0.5%, as measured by X-ray photoelectron spectroscopy (XPS). The specific surface areas of the CNFs and CNTs were 150–200 m^2/g and 300 m^2/g, respectively, as measured using the Brunauer, Emmett, Teller method (BET). Both types of nanofillers were supplied in the form of dry powders.

Unidirectional carbon fibre/epoxy laminates were used as substrates, and they were manufactured by the Instituto Nacional de Técnica Aeroespacial (INTA, Spain) by stacking unidirectional prepregs (Hexply 8552/33%/268/IM7-12K, supplied by Hexcel). The curing was performed in an autoclave with vacuum bag at 180 °C for 2 h at a pressure of 6 bar.

2.2. Manufacturing of the nanoreinforced adhesives

To achieve a good dispersion of the carbon nanofillers in the epoxy matrix, the nanoreinforced adhesives were processed using several steps. The CNFs and CNTs were dispersed in DGEBA following a procedure that includes the use of a solvent, ultra-sonication and mechanical stirring. The solvent (chloroform) and the dispersion conditions were selected in a previous work [26]. The nanofillers were first dispersed in chloroform at 45 °C for 30 min. Then, DGEBA was added to the mixture, which was then mechanically stirred at 150 rpm for 30 min at 45 °C and sonicated for 45 min at the same temperature with a 50–60 Hz ultrasonicator. Subsequently, the DGEBA–nanofiller–chloroform mixture was degassed at 90 °C for more than 12 h to eliminate the remaining solvent and the trapped air. Because the carbon nanotubes in the adhesive are amino-functionalised, a pre-curing

treatment (heating at 150 °C for 1 h) was applied to induce the chemical reaction of these functional groups with the epoxy monomer before curing. Finally, a stoichiometric amount of the hardener was added. The curing process for the neat and reinforced adhesives was performed in two steps: 3 h at 150 °C and then 1 h at 180 °C. The obtained glass transition temperatures (T_g) were 169 °C for the epoxy, 160 °C for the CNF/epoxy and 157 °C for the CNT/epoxy adhesives, as measured by differential scanning calorimetry (DSC) [27].

Only one concentration was used for each type of nanofiller: 0.50 wt% CNF and 0.25 wt% CNT. These concentrations correspond to 0.30 and 0.16 vol% for the CNFs and CNTs, respectively, based on the density values provided by the manufacturers. These concentrations were selected based on previous studies on the joint strength and properties of the adhesive [21,28].

2.3. Surface treatment of the substrates

Three different surface treatments were applied to the laminates before the adhesive bonding: peel ply, grit blasting and atmospheric pressure plasma. The use of a peel ply is a very common treatment for carbon fibre/epoxy laminates. This treatment involves placing a ply over the last layer of the prepreg before curing. In this case, we selected a dry polyester peel ply (Release Ply C, Airtech). This ply is a weave composed of groups of 16–18 fibres that are 15 μm in diameter. The ply was removed immediately before bonding to generate a rough surface that was free of contamination.

Dry grit blasting was performed by hand using a Guyson (mod. Jetstream 22, North Yorkshire, England) grit blaster with 220 grit alumina (diameter in the range of 60–70 μm). Three passes were performed with the gun at an angle of approximately 45° and a distance of 10–15 cm from the surface of the composite. The grit blasted surfaces were then cleaned with acetone and compressed air to remove the alumina particles that remained on the surface after the treatment.

The atmospheric plasma treatment was performed using a plasma system supplied by PlasmaTreat (Elgin, IL, USA). The samples were placed on a moving platform (1.2 m/min) in such a way that the distance between the surface of the laminate and the plasma nozzle was 7 mm. The treatment power was 615 W. Only one pass was made because the diameter of the plasma beam (25 mm) is almost the same as the width of the laminate substrate (25.4 mm).

2.4. Characterisation

The water uptake of the adhesives was determined by periodically weighing the adhesive specimens (manufactured by moulding, with a size of $35 \times 12.5 \times 1.7$ mm^3) using a Mettler Toledo AX205 digital balance (Zürich, Switzerland) with a 10^{-5} g resolution. The percentage of water gain was determined from the equation:

$$M_t = \frac{W_t - W_0}{W_0} \cdot 100$$

where M_t is the absorbed water at time t, W_t is the mass of the specimen at time t and W_0 is the initial mass. The diffusion coefficients were calculated using a simplification of Fick's law, which was proposed by Crank [29]:

$$\frac{M_t}{M_s} = \frac{4}{h} \cdot \sqrt{\frac{D \cdot t}{\pi}}$$

where M_s is the absorbed water when the polymer is saturated, D is the diffusion coefficient and h is the thickness of the specimen.