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Micro-scale modeling of water diffusion in adhesive composite joints

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ABSTRACT

Water diffusion into composite adhesive joints was experimentally studied by means of gravimetric measurements in bond specimens. The main parameters controlling the diffusion in the bond components were obtained from water uptake experiments carried out in bulk specimens of fiber-reinforced composite and epoxy adhesive. The diffusion of water in bonds is a complex mechanism due to the heterogeneous microstructure of the composite and its interface with the adhesive. This process was simulated through microscale models which represent the microstructure of the composite and of the adhesive joint. Numerical simulations were able to accurately predict the mass gained due to the water uptake and the mechanisms of diffusion through the composite microstructure. These models were employed to evaluate the influence of the geometry and of the material properties on the diffusion of water in a representative composite joint.

1. Introduction

Compared with conventional mechanical joining techniques, the use of adhesive bonds presents numerous advantages such as a more homogeneous stress distribution, higher stiffness, high fatigue strength, low weight, the possibility to join dissimilar materials or corrosion prevention [1]. For these reasons, structural adhesive bonding has been increasingly used in industries including construction, automotive and sports. However, in spite of the expected weight reductions, the use of adhesive composite bonds in aeronautical applications is limited by the possible deterioration of the joint upon exposure to environmental contaminants and the lack of adequate techniques to monitor the quality of the bond.

The identification of the harmful factors and contaminants affecting the performance of composite joints for aeronautics applications has not been fully achieved. Furthermore, their presence cannot be easily detected by conventional non-destructive tests (NDT). Hence, Markatos et al. [2] identified significant degradations in the fracture toughness of bonded joints in five different harmful scenarios: moisture, release agent and Skydrol contamination, effect of the curing process and high temperature during service.

Moisture contamination is probably the most studied scenario for bulk polymers and composite materials [3–6], and numerous models have been proposed to adequately describe this process [7–9]. The ASTM standard for water diffusion in thin plates of fiber reinforced polymers (FRP) [10] considers that this process can be adequately described by the one dimensional Fick's second law, which is given by:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{1}$$

where c is the moisture concentration, D is the diffusion coefficient, t is the time and x is the position through the thickness. A useful closed-form approximate solution is given as [11]:

$$\frac{M(t)}{s} \approx 1 - \exp\left[-7.3\left(\frac{Dt}{h^2}\right)^{0.75}\right] \tag{2}$$

where $M(t)$ is the evolution of the water absorbed, s the water content at saturation and h the thickness of the plate.

Fick's law is the simplest model to describe the diffusion of water into a material. However, moisture absorption in epoxy adhesives cannot usually be accurately described with this model [12,13]. Thus, more elaborated diffusion theories are required to reproduce the experimental moisture-uptake curves. The most widely accepted diffusion models to reproduce the water absorbed in polymers can be divided in two groups: multiphase diffusion (Langmuir model) and time-dependent diffusion. The Langmuir diffusion model was developed to deal with two phases of different diffusion kinetics. This model assumes that water can diffuse into the material, but some water molecules are also trapped inside the epoxy microstructure. This behavior is described by:

$$\frac{\partial c_f}{\partial t} + \frac{\partial c_b}{\partial t} = D\frac{\partial^2 c_f}{\partial x^2} \tag{3}$$

$$\frac{\partial c_b}{\partial t} = \gamma c_f - \beta c_b \tag{4}$$

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where subscripts f and b stand for the free and bounded water phases, respectively. The parameters γ and β control the probability of water in each state. As for the Fickian model, the solution can be approximated by [14]:

$$\frac{M(t)}{s} \approx \frac{\beta}{\gamma+\beta}\exp(-\gamma t)\left\{1-\exp\left[-7.3\left(\frac{Dt}{h^2}\right)^{0.75}\right]\right\}+\frac{\beta}{\gamma+\beta}\times[\exp(-\beta t)-\exp(-\gamma t)]+[1-\exp(-\beta t)] \tag{5}$$

Time-dependent diffusion models are supported by the experimental data which show that both saturation and diffusivity are clearly stress-dependent in some polymers [15]. Therefore, the deviation from the Fickian behavior in glassy polymers could be related to the viscoelastic relaxation of the polymer which may change its response to the absorption of penetrant molecules [16]. Thus, the experimental behavior deviates from the Fick's prediction when the viscoelastic relaxation rate is comparable to the water diffusion rate. Based on this assumption, Roy et al. [17] suggested that the viscoelastic effects can be modeled through a diffusivity coefficient varying with time. Alternatively, Cai and Weitsman [18] proposed time-dependent boundary conditions to reproduce the water uptake data in epoxy resins. All the aforementioned models are able to fit the experimental water uptake curves in terms of weight gain. However, LaPlante et al. [14] used nuclear resonance imaging of deuterated water into a polymer to demonstrate that the moisture distribution through the thickness of the specimen could be more adequately fitted by considering time-dependent boundary conditions. For this reason, this later approximation was selected in this work for the numerical simulations of the water absorption in the adhesive specimens.

There are many different configurations of composite adhesive bonds to minimize peel stresses and maximize the strength of the joint [19,20]. However, for any possible joint configuration, the ideal geometry consists in two or more composite parts joined by a thin adhesive layer (0.10–0.30 mm thick) which transmits the efforts in shear. Thus, the adhesive surface directly exposed to the environment is very small and the direct water diffusion into the adhesive could be almost neglected. However, in spite of the low diffusion rate in FRP, water can still diffuse through the composite adherents and contaminate the adhesive joint. The diffusion of water through the composite face sheets has been observed as an important degradation mechanism in composite/foam sandwich structures [21,22] and adhesive composite joints [23]. Adequate models to represent the diffusion of water in composite bonds should include full details of the microstructure. Finite element models which take into account the composite microstructure have recently shown their potential to predict the water diffusion in unidirectional laminates [24,25]. These simulations can also be applied to study the mechanisms of diffusion in composite bonds.

In the present work, the water diffusion through composite bonds is experimentally and numerically investigated. Gravimetric methods are applied to determine the parameters controlling the water uptake in adhesive, composite and bonded specimens. Experimental results are compared with analytical and numerical models. Finite element simulations which take into account the heterogeneous microstructure in the composite adherents are able to reproduce the mechanisms of diffusion in adhesive composite joints.

2. Materials and experimental techniques

The FRP used in this study was M21/T700, this material is considered by Airbus as a future application-relevant composite [2]. HexPly M21 is a high performance epoxy resin designed by Hexcel with outstanding toughness and excellent damage tolerance. This resin was supplied as pre-impregnated plies combined with unidirectional high-strength carbon fibers (T700 from Toray). The selected structural adhesive was the film Cytec FM-300 K0.5. This is a modified epoxy adhesive with a polyester carrier wide open knit which combines high strength and toughness with excellent environmental resistance. This adhesive is commonly used to bond metals, composites, metal to composite or honeycomb sandwich structures and it is selected as a structural adhesive for aeronautical applications [26].

Several plies of the adhesive film FM-300 K were stacked to manufacture two rectangular specimens for water uptake measurements. The adhesive was heated at 3 °C/min and consolidated at 175 °C in the autoclave under 3 bar pressure for 60 min. Before achieving the curing temperature, a vacuum outgassing step at 110 °C for 30 min was applied to minimize the porosity of the specimen [27]. Differential scanning calorimetry (DSC) analysis was carried out using a DSC TA Q100 under the form of heating ramps from 20 to 250 °C at 10 °C/min to confirm that the adhesive was fully cured after this curing cycle. The evolution of the heat flow in a cured specimen of FM-300 K is plotted in Fig. 1. Heat flow shows a quasilinear evolution between ≈20 and 150 °C, without presence of any residual heat of reaction. The glass transition temperature could be related with the change in the slope of the curve at ≈160 °C. The exothermic process appearing at temperatures higher than 200 °C showed the thermal degradation of the polymer and most probably the onset of melting of the polyester carrier yarn. The specimens were visually inspected by holding each sample up to a negatoscope to detect possible macroscopic defects, additional metallographic samples were prepared and observed in the optical microscope to ensure that the cured material was free of microscopic defects. The final dimensions of the adhesive specimens were ≈13 × 13 × 1.25 mm^3.

Water absorption experiments were conducted on unidirectional specimens of M21/T700 CFRP according to the recommendations of the ASTM standard for the determination of the absorption properties in composite materials [10]. Two CFRP specimens were manufactured by stacking five plies of M21/T700 prepreg and consolidated in the autoclave under 7 bar pressure and 180 °C during 120 min. The thickness of the specimen was accurately measured through the microscopic inspection of the specimen cross section. The dimensions of the specimens were ≈100 × 100 × 1.1 mm^3.

The experimental study of the water diffusion in adhesive composite joints can be made difficult by the low diffusion rate of the adherents, which implies extremely long-term experiments. In order to accelerate the process, the bonded specimens were manufactured with very thin CFRP parts obtained from a unidirectional

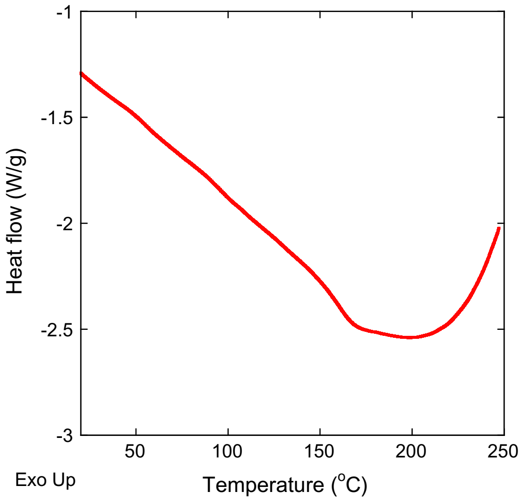

Fig. 1. DSC results for FM-300 K cured in the autoclave at 175 °C and 3 bar pressure.