Water Resistance of Glass Fibre Reinforced Epoxy (GFRP) and Carbon Fibre Reinforced Epoxy (CFRP) Composite

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1.   Introduction

Currently thermoset and thermoplastic materials reinforced with fibres or metals are widely applied in all kinds of high performance applications, and their application will grow considerably in the near future. Their low weight, mechanical strength and chemical resistance make them attractive construction materials.

The epoxy resins evaluated in this paper, and many modern polymers in general, have an intrinsic chemical resistance against water. This means that surface corrosion by water, in contrast to most metals, is not a very important issue. Of greater interest is the effect of water that diffuses into the epoxy resin, and reaches the epoxy - fibre interface and the macromolecular object: the fibre. Due to interaction of water with the interface and fibre, lagged chemical degradation of the composite is a realistic scenario. This paper focuses on this subject. With this regard a glass fibre reinforced epoxy composite (GFRP) and a carbon fibre reinforced epoxy (CFRP) composite are evaluated.

2.   Background

In recent years many researchers have focused on the mechanical properties of the epoxy-fibre interface in moisture free situations [1] or in case the material was saturated with water [2]. Furthermore, the work of Kinloch [3] considers interface issues from the viewpoint of applied chemistry. Walter and Ashbee [4] evaluated the growth of a blister due to interface problems and osmosis. Remarkably, more fundamental work was carried out more than twenty years ago. This is understandable: composites and coatings have been improved for an important extent since then, and most consumer goods function reasonably well during the general accepted service life. Apart from the fact that these goods are not exposed to extreme circumstances as in some chemical processing operations, the required life time is generally less than for aerospace structures or civil engineering applications.

At this point, it is noteworthy that seemingly unexplainable anomalies are still noticed on a laboratory scale, such as loss of polymer - fibre adhesion strength, unexpected decrease in overall composite mechanical performance, composites that seem to leach chemicals and take up water afterwards, and so on. For a long service life it is inevitable to acquire the possible root causes for these phenomena, also because more aggressive chemicals than water, such as acidic and alkaline aqueous solutions, may come into play in new applications.

In this paper the effects of a possible chemical reaction with the matter that facilitates the interface, so called sizing, is evaluated. The degradation of the fibre itself is not evaluated as this seems to be a minor issue in case of water. The main question is: can a macroscopic solution be formed as a result of reaction or by intrinsic poor adhesion, giving rise to an osmotic pressure with subsequent (micro) blister formation? Such a growing blister could alter the dimensions of the composite, hereby giving rise to (micro) cracks and leaching of water and composition material through the blister surface or along the fibre. To answer this question, the solubility and swelling behaviour of the different materials are described; secondly the epoxy - fibre interface is analyzed; finally the thermodynamics and mass transfer of blister growth are evaluated.

3. Solubility and Swelling

Water uptake of a high performance epoxy resin is between 1 and 2 volume percent at 300 Kelvin. From cast epoxy resins and many other resins, such as vinyl ester resins, it is known that after reaching pseudo equilibrium, they tend to take up some additional water rather slowly. Subsequently a final equilibrium is reached. Without going into much detail on this relaxation mechanism, it should be noted that in case of epoxies that have a relative low polarity, the final equilibrium that is reached does not exceed the available free volume [5]. Because of this, the dimensional change of cast epoxy resin due to the water uptake is negligible.

Fibre sizing also absorbs water. In case of glass fibre composites often silane based sizings (adhesion promoters) are used. From these sizings it is known that they take up water and are simultaneously hydrolyzed by water, even at room temperature [3]. Silane based sizing is not unique in that respect. From other kinds of adhesives, such as poly-vinylacetate it is also known that they are hydrolysed [6]. However, epoxy sizing on carbon fibres is expected to be hardly susceptible to degradation by water due to the chemical nature.

Water solubility in the sizing is usually higher than solubility in the matrix material. With this in mind it could be hypothesized that water induced swelling of sizing may cause the dimensions of the composite to alter. However, as the amount of sizing is limited and the free volume available in sizing is considerable, due to the specific molecular orientation of sizing, it is not expected that swelling of sizing occurs. This reason will be explained more thoroughly below. So far, we can conclude that in the following evaluation it makes sense to exclude swelling effects with regard to epoxy resin and sizing.

4. Epoxy - Fibre Interface

As the epoxy-fibre interface is of major interest, in this paragraph the applied chemical and mechanical properties are described.

The volume of fibres in an aerospace composite is around 50 vol.%. The volume of sizing on a fibre is 2 vol.%. This results in an interface volume of 1% on the total composite. According to Kinloch [3] the interface consists roughly of three different layers: a fibre/sizing interface with covalent chemical bonding; an interphase of oligomers with increasing crosslink density towards the fibre/sizing interface and the sizing/epoxy interface with covalent chemical bonding. The oligomer phase may be the place where a microscopic solution due to a reaction with water could be formed.

From reference [2] it is known that the initial interfacial strength of a glass fibre epoxy with silane sizing is 27 MPa. For an epoxy with epoxy sized carbon fibres this is around 100 MPa. Koenig and Emadipour [7] showed that interfacial shear strength of silane sizing reduces by around 70% in 30 days on immersion in water at 298 Kelvin. After 270 days, this levelled out to a constant reduction of almost 96%. For epoxy sizing less data is available, however when the epoxy sizing is properly cured it is, as stated, expected to be much less susceptible to hydrolysis. This is confirmed by the fact that epoxy - carbon shear strength reduces much less: around 10% at 353 Kelvin in an environment with 95% humidity [2].

5. Blister Formation Theory

Whether a blister will grow depends on (i) the generated osmotic pressure at some point in time (ii) the interfacial epoxy - sizing strength and (iii) the elastic force of the composite. The condition for growth can be determined by use of a Gibbs energy balance that contains these three factors. If the blister can grow, the growth rate is usually determined by the diffusion rate into the blister. By means of a mass balance and the Maxwell-Stefan diffusion equation, we can simulate the growth rate. However, before doing this, one must realize that the moment that osmotic pressure becomes apparent is most often determined by diffusion time lag. Below we will first discuss time lag in more detail, then we will describe the energy balance and mass balance for blister formation thoroughly.

5.1 Time Lag

When the composite is contacted with water, water will slowly permeate. The penetration depth is estimated from [8],[9]:

$$z = \sqrt{\pi \cdot D \cdot t} \tag{1}$$

From formula (1) the penetration time lag can be calculated. Only after this time, when water has reached the fibres closest to the surface, the blister will start to grow.

5.2 Blister Gibbs Energy

The work from Walter and Ashbee [4] for composite cracks that are initiated by penny shaped blisters, serves as a base for the developed Gibbs energy balance for micro blister formation. For blister expansion, the energy balance contains a term for the change in interfacial surface energy and one for the elastic energy of the epoxy. The change of surface energy can be expressed as follows:

$$dG_{surface} = -\overline{\sigma} \cdot dA \tag{2}$$

It is assumed that the surface energy $(\overline{\sigma})$ of the carbon - epoxy interface is 0.03 J/m^2. The glass - epoxy bond has a much lower strength. The energy has been taken as 0.001 J/m^2, as we account for the strong loss of local adhesion due to water reaction with fibre sizing. The surface energy is negative because it opposes the direction of the blister growth. The term for the change in elastic energy for the hemispherical blister is defined by:

$$dG_{elastic} = \tfrac{2}{3} \cdot p \cdot z \cdot \left(\frac{p}{E}\right) \cdot dA \tag{3}$$

The resulting total energy expression has a minimum for a certain blister size. This minimum defines an equilibrium condition, which we express in terms of critical pressure:

$$p_{crit} = \sqrt{\frac{2 \cdot \overline{\sigma} \cdot E}{d}} \tag{4}$$

If the osmotic pressure becomes equal to - or smaller than - the critical pressure, the blister reaches equilibrium in the specific process conditions. Subsequently, blister growth ends.

5.3 Maxwell-Stefan Mass Transfer

We assume that blister growth is governed by a semi-stationary form of the Maxwell-Stefan equation for mass transfer [10]. This takes the chemical potential gradient as the driving force. Here this contains two terms due to composition and pressure gradients. The one-dimensional form of this equation is:

$$N_w = c_w \cdot D \cdot \left[\frac{dx}{dz} + \frac{\overline{\upsilon_w} \cdot \overline{x_w'}}{R \cdot T} \cdot \frac{dp}{dz} \right] \tag{5}$$

$$\approx c_w \cdot D \cdot \left[\frac{x_w - x_w''}{\Delta z} + \frac{\overline{\upsilon_w} \cdot \overline{x_w'}}{R \cdot T} \cdot \frac{\Delta p}{\Delta z} \right] \tag{6}$$

The diffusion distance is taken to be that from the composite surface to the first fibre.

6 Blister Formation Simulation

Performance carbon fibres have a thickness of around 6 micrometer and carry around 2 volume percent of sizing, giving a layer thickness of 0.1 micrometer. The size of the nucleus that initiates the osmotic process is hard to determine. For our calculations we conservatively assume that the initial nucleus base diameter is also 0.1 micrometer. This nucleus contains water and sizing reaction products. The initial ratio of these species depends on the reaction equilibrium condition. In case of a silane based sizing that is used for glass fibres, the equilibrium constant is around 0.8. In case of the epoxy sizing on carbon fibre it is expected that the equilibrium constant is larger than 0.99 at 300 Kelvin. To simplify the formulae we assume that the reaction products have the same density and molar mass as water.

Knowing all parameters that are required for our calculations, we can depict the osmotic pressure and the critical pressure as a function of blister diameter. Below the results for the two composites are depicted.
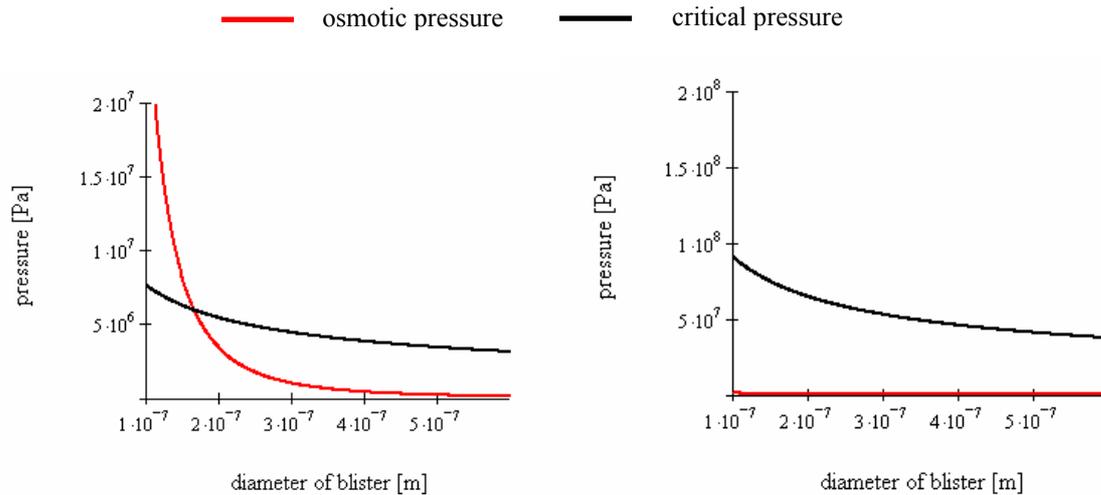
Graph 1: Pressure profiles for a growing blister. Left picture is for a glass fibre - epoxy composite. Right is for a carbon-epoxy composite. For the material in the right graph, it can be noticed that the critical pressure is too large to allow any blister growth.

Using the Maxwell-Stefan equation and the appropriate mass balance, the blister growth in glass fibre - epoxy is simulated. The epoxy thickness in front of the fibres is 3 mm. The diffusion coefficient is 9 x 10^{-13} m^2/s at 300 Kelvin. The penetration equation gives a significant time lag[1]. Below the growth is shown.
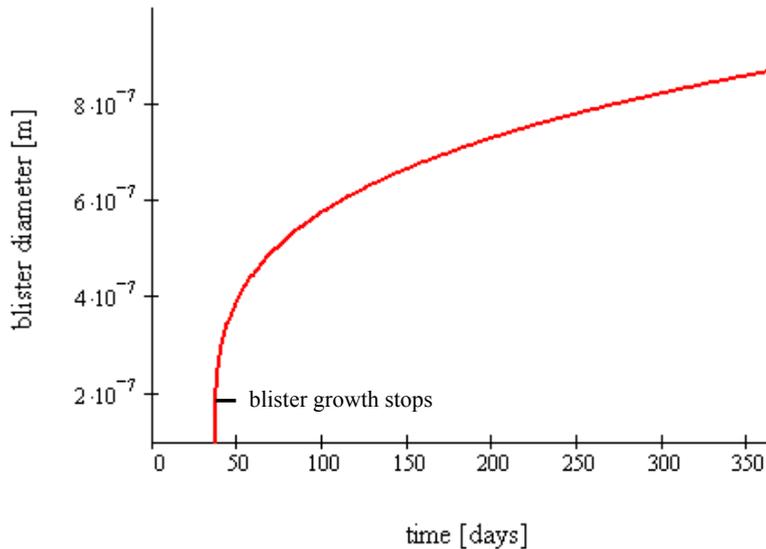
Graph 2: Hemispherical blister diameter as a function of time.

The blister growth will stop when the diameter has become around 0.2 micrometer. This is only twice the initial size in the process conditions simulated. Note that this size is reached almost instantaneously after the calculated time lag.

7   Conclusion

Although the glass - epoxy composite has some potential of blister growth, it can be noticed that cracking effects may be limited at 300 Kelvin, while the blister dimensions remain small. However at higher temperature, for example at 370 Kelvin, the blister growth will continue longer. This will mainly be caused by reduction of the opposing pressure from the composite. This conclusion is qualitatively in line with the research of Chateauminois et al.[11]. Last but not least, we must mention that we did not evaluate the effect of rapid changes of temperature and sub-zero temperatures.

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[1] Laboratory samples usually have more fibres located near to the outside surface.

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