Tensile behaviour of stainless steel fibre/epoxy composites with modified adhesion

Michaël Guy Callens [a,*], Larissa Gorbatikh [a], Ellen Bertels [b], Bart Goderis [b], Mario Smet [b], Ignaas Verpoest [a]

[a] Department of Materials Engineering, KU Leuven, Belgium
[b] Chemistry Department, KU Leuven, Belgium

ABSTRACT

In this study we investigate the tensile behaviour of unidirectional and cross-ply composites reinforced with ductile stainless steel fibres and modified adhesion to the epoxy matrix. Results show that annealed stainless steel fibres have a potential in designing tough polymer composites for structural applications. The stiffness of the UD composites made from these fibres is 77GPa combined with the strain-to-failure between 15% and 18% depending on the level of adhesion. Silane treatments were used to modify the adhesion. By treating the stainless steel fibres with different silane coupling agents, an increase of 50% in the transverse 3-point-bending strength was realised. Increasing the adhesion by 50% leads to a higher tensile strength and strain-to-failure in both UD and cross-ply laminates and a higher in-situ strength of the 90° plies. It also delays formation of matrix cracks and hinders growth of debonding.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The strain-to-failure of structural polymer-matrix composites can be enhanced by using more ductile fibres as reinforcement, but most known fibres with higher strains-to-failure such as polymeric [1–4] and natural fibres [5–10] are not stiff enough to compete with carbon and glass. Fibres that simultaneously combine high stiffness and high strain-to-failure are difficult to find. A new type of fibre recently became available for use in composites – stainless steel fibres with stiffness of ∼193 GPa, strain-to-failure of ∼20% and diameter of 30 μm or less. Steel fibres are unique in the sense that their strain-to-failure can be altered in a wide range without affecting their stiffness.

Previous research [11–15] has shown that composites made from these fibres possess a high stiffness and a high strain-to-failure. In [11] the authors show that the strain-to-failure can be further increased if the matrix material has a higher ductility. In [15] a ductile epoxy (±8% strain-to-failure) has been used to produce composites with a strain-to-failure up to 19%. The importance of an optimised fibre/matrix interface in stainless steel fibre composites was emphasized in [11,15], where it was reported that all stainless steel fibres were locally debonded from the matrix. Despite these observations, no work has yet been published on

the tensile properties of steel fibre composites with a modified fibre–matrix interface.

The fibre–matrix interface plays an important role in controlling the mechanical behaviour of composites. If the matrix is more brittle than the fibres, it can strongly influence the tensile properties of composites in the fibre direction [16–19]. A higher adhesion may hinder the development of matrix cracks and lead to a higher strength and strain-to-failure of the composite [20]. In the case of a too high adhesion, however, the cracks may result in localization and magnification of the strain, which is likely to cause earlier failure of the fibres [16,17]. Thus, an optimal level of adhesion is sought.

The adhesion strength is also important for transverse properties of UD composites. Since stainless steel fibres are isotropic and have very high stiffness, the mismatch between the stiffness values of stainless steel and polymer is about two orders of magnitude. This creates very high stress concentrations at or near the fibre/matrix interface [21], which can lead to an early onset of matrix cracks. By increasing the interface strength, this onset of matrix cracks can be delayed.

The adhesion can be modified with coupling agents. For a durable bond between polymeric and inorganic materials, silane coupling agents are most commonly used [22,23]. While the properties and quality of silane layers strongly depend on the deposition conditions and can vary greatly between applications, it is generally accepted that coupling of a metal and a matrix through a silane often results in better adhesion and durability

---

* Corresponding author.
  E-mail address: michael.g.callens@gmail.com (M.G. Callens).

compared to direct application of the matrix on the metal. Many studies reported an increase in adhesion strength when using silanes to construct metal-polymer joints, which can be up to more than 100% stronger compared to untreated joints [23–28].

A universal silane that can be applicable to all metals and matrices and useful for all purposes does not exist. Silanes differ in physical and chemical characteristics. There are some silanes that are referenced in the literature more often because of their excellent properties. These include 3-glycidoxypropyltrimethoxysilane (GPS), 3-aminopropyltriethoxysilane (APS), and bis-silanes, especially 1,2-bis-(triethoxysilyl)ethane (BTSE) [29].

In this research, GPS, APS and BTSE silane coupling agents are deposited on the fibre surface using wet chemical methods. Unidirectional (UD) and cross-ply (0, 90) s stainless steel fibre/epoxy laminates are produced using a vacuum assisted resin infusion process. The produced composites are tested in transverse 3-point bending and in a quasi-static tensile test to assess the effect of the adhesion modifications.

2. Materials and methodology

2.1. Reinforcement and matrix materials

A woven quasi-unidirectional (Q-UD) structure consisting of stainless steel fibre weft yarns and thin thermoplastic polyethylene terephthalate (PET) warp yarns (Fig. 1) is supplied by NV Bekaert SA (Belgium). The thin PET warp yarn is used to minimise the crimp in the steel fibres while stabilizing the architecture. The areal density of the weave is 1425 g/m^2. The annealed stainless steel fibres are made of a 316 stainless steel alloy and are produced using a bundle drawing technique, in which multiple stainless steel wires are combined in a copper matrix and subsequently drawn to smaller diameters [30]. After drawing the copper matrix is removed and the final diameter of the fibres is 30 μm.

The matrix is an Epikote 828LVEL (a Bisphenol-A type) epoxy resin with a 1,2-diaminocyclohexane (Dytek DCH-99) as hardener to be used in ratio 100/15.2. Mechanical properties of the stainless steel fibres and the epoxy matrix are previously reported in [11].

2.2. Modification of the stainless steel fibre surface

Stainless steel fibre fabric is treated with silane coupling agents to establish a covalent chemical bridge between the stainless steel surface and the epoxy matrix. The deposition is done by dipping the stainless steel fibres into an alkoxysilane solution in a water/alcohol mixture. The alkoxysilane molecules in solution need to be sufficiently hydrolysed before they can attach to the stainless
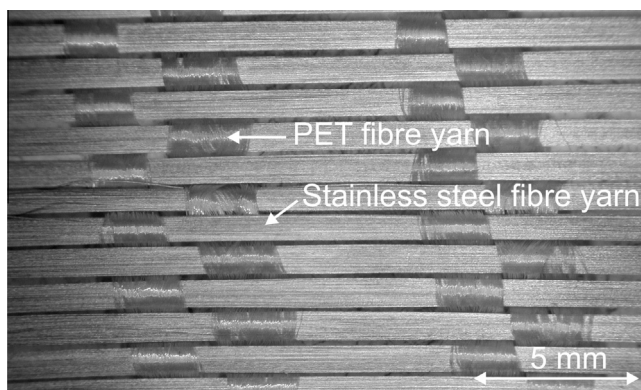
steel surface by condensation of hydroxyl groups, while self-condensation in solution should be minimised (Fig. 2a and b).

The silanes used in this study are shown in Fig. 2c: 3-Aminopropyl-triethoxysilane (APS) and 3-glycidoxypropyltrimethoxysilane (GPS) were purchased from Acros Organics, 1,2-bis(triethoxysilyl)ethane (BTSE), acetic acid and deuterated solvents for NMR measurements from Aldrich.

Before deposition of the silanes, the stainless steel fibres were cleaned ultrasonically in ethanol for 15 min. After rinsing them in water and air drying, the stainless steel fibres were dipped in the alkoxysilane solutions and briefly rinsed in ethanol. The APS solution was prepared from a 90/10 (v/v) water/ethanol mixture to which 2 v% silane was added. The GPS solution was prepared analogously, but the mixture was acidified with acetic acid up to pH 5. The BTSE solution was prepared starting from a 50/50 (v/v) water/ethanol mixture and also acidified with acetic acid. These solutions were stirred until maximum hydrolysis was reached. Hydrolysis and self-condensation were checked using NMR.

After deposition, APS and GPS condensation to the substrate occurred by 4 h of condensation in a vacuum oven at 90 °C. In the case of combination with BTSE, the latter was first deposited on the substrate, dried for 1 h at 90 °C in a vacuum oven, after which APS was applied as described above. The composites were produced within 1 h after drying the coated fibres in a vacuum oven to eliminate aging effects of the coating.

2.3. Composite production

Three layers of the quasi UD structure were stacked for the UD laminate. Four layers were stacked for the cross-ply laminate in (0, 90) s lay-up. The composite plates were produced using a vacuum assisted resin infusion process. The impregnation was done at 40 °C and the epoxy was cured for 1 h at 70 °C and post-cured for 1 h at 150 °C.

The quality of the produced laminates was investigated using optical microscopy. Good impregnation was achieved with no voids or defects detected. The thickness and the fibre volume fraction of the laminates are listed in Table 1. Fibre volume fraction is calculated based on the thickness and areal density of the fabric. The APS coated UD laminated showed a significantly lower fibre volume fraction in comparison with the reference composite (i.e. with untreated fibres). This was possibly due to minor misalignment of the fabrics which prevented nesting of different layers. For the cross-ply composites, no difference was found between treated and reference laminates.

Fig. 3 shows a cross-section of the reference UD laminate. Fibres are tightly packed inside yarns with a quasi-hexagonal packing. This seems to be a result of the bundle drawing process by which the fibres are produced. Their close packing is largely retained even after copper is removed. Due to this, the fibre volume fraction within a yarn is on average 75.8 ± 2.2% (based on image analysis of composite cross-sections). Despite the high fibre volume fraction inside yarns, they were well impregnated.

2.4. Experimental methodology

The transverse 3-point bending test was performed according to ASTM D790 on an Instron 4467. The test speed was 1 mm/min. Sample width was 10 mm and the span length was 50 mm.

The UD and cross-ply samples were additionally tested under quasi static tensile loading. The tests were performed according to ASTM D3039 on an Instron 4505. The displacement was controlled to 2 mm/min and the force was measured using a 100 kN load cell. Sample width for the UD tensile samples was 15 mm and for the cross-ply samples 25 mm. The gauge length was 150 mm and no end tabs were used. The strain interval for

Fig. 1. Photograph of the quasi-unidirectional stainless steel fibre woven structure.