Composites Science and Technology 167 (2018) 32–41

Contents lists available at ScienceDirect

Composites Science and Technology

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

# Reaching maximum inter-laminar properties in GFRP/nanoscale sculptured aluminium ply laminates

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ARTICLE INFO

*Keywords:*
A. Hybrid composites
A. Metals
B. Delamination
B. Surface treatments
E: Resin transfer moulding (RTM)

ABSTRACT

The aim of the present work is to reach maximum inter-laminar properties in fibre metal laminates (FML) consisting of glass fibre reinforced polymer (GFRP) and aluminium (Al) plies. The Al plies are AA5019 and AA5754 alloys and pre-treated by nanoscale sculpturing before the FMLs are manufactured by resin transfer moulding. The nanoscale sculpturing of the Al plies leads to the formation of cubical hook-like structures on the surface giving rise to a three-dimensional mechanically interlocking surface. The inter-laminar properties of the FML are investigated by double-notch shear as well as double cantilever beam (Mode I) and end notched flexure (Mode II) testing methods and compared to untreated Al plies and conventional GRFP laminates as reference. As result the nanoscale sculptured Al plies show drastically increased inter-laminar mechanical properties due to highly improved inter-ply bonding between metal surface and resin. For all FMLs with nanoscale sculptured Al plies the delamination appears in the transition zone between glass fibres and matrix due to the lower adhesion of the glass fibre/matrix interface compared to the nanoscale sculptured Al ply/matrix interface. This proves that the maximum necessary inter-laminar properties are achieved.

## 1. Introduction

Delamination is one of the most common degradation mechanisms in fibre reinforced polymer (FRP) laminates and occurs due to low inter-laminar strength. Defects in structures, such as impact damages, which may occur during the manufacturing process as well as in service, can lead to delamination between adjacent layers. This has a significant influence on the mechanical properties and leads often to catastrophic failure of the composite. The choice of fibre and matrix types, the lay-up, the properties of the composite constituents and in particular the inter-ply bonding, which is affected by fibre surface pre-treatment, plays an important role for the failure mechanisms. Increasing the inter-ply bonding improves the resistance to crack propagation of an inter-laminar interface and prevents early delamination. Consequently, it leads to a higher mechanical performance [1–5]. Coupling agents such as silane are often used to increase the interfacial adhesion of fibre/matrix [6].

A need for improved material properties resulted in development of hybrid composites of stacked thin metal sheets and FRPs. Fibre metal laminates (FML) combine the superior fatigue and fracture characteristics of FRPs with the ductility and durability offered by many metals. Most of these hybrid composites are manufactured by prepreg-autoclave technology [3,7–10]. Allaer et al. [11] investigated the in-plane mechanical properties of unidirectional (UD) stainless steel fibre/epoxy laminates under quasi-static tensile, compression and shear loading experimentally. Fracture surfaces showed no presence of matrix adherence on the steel fibres, indicating low fibre/matrix interfacial strength. Callens et al. [12] studied the influence of silanisation as adhesion promoter in UD and cross-ply stainless steel fibres/epoxy composites. Silanisation led to increased interfacial strength, higher toughness, higher strain-to-failure and dissipated energy compared to conventional laminates. The fracture surface showed a mixed mode of adhesive and cohesive failure, although adhesion predominated.

Further conventional methods to improve the Al/polymer adhesion involve chemical surface structuring techniques. These divide into chemical etching (acidic or alkaline solutions) and anodisation. Chemical Al etching is typically conducted in acids like chromic acid or in alkalines like sodium hydroxide [13]. Here, defects being specific to the surface (e.g. mechanical damages after cutting, sand blasting or polishing) are preferentially attacked creating an increased surface

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https://doi.org/10.1016/j.compscitech.2018.07.033
Received 23 August 2017; Received in revised form 7 May 2018; Accepted 21 July 2018
Available online 24 July 2018

roughness. This usually also includes preferential dissolution of the grain boundaries weakening the near-surface microstructure. Anodising is conventionally performed in acidic electrolytes like chromic acid or phosphoric acid under potentiostatic conditions [14] forming oxide layers on the Al surface with a thickness up to several microns and drastically increased surface roughness [15]. These oxide layers tend to exhibit effects of crazing under thermal and mechanical load, weakening the mechanical stability of the oxide layer [16].

The nanoscale sculpturing technique used in the present work overcomes these difficulties generating a three-dimensional mechanical interlocking structure on the Al surface based on the intrinsic properties of the surface-near microstructure [17]. This technique combines the formation of intermediate oxide layer in the nanoscale and its subsequent dissolution. Thus, the grains and planes oxidising slowest are emphasised, so that the most chemically and mechanically stable surface is created without any preferential grain boundary dissolution.

There are several methods to characterise the inter-ply properties of composites. The standard test method: double cantilever beam (DCB) and end notched flexure (ENF) are employed to determine the energy release rates $G_{Ic}$ (Mode I) and $G_{IIc}$ (Mode II), respectively. Different experimental studies have indicated that the most conservative inter-laminar toughness values are produced by testing unidirectional laminates in which the delamination propagates along the fibre direction between the plies. The 0° plies in these laminates often produce fibre bridging, which influences the toughness values [18–21]. It was shown, that a crack in laminates with multidirectional plies have a tendency to propagate through neighbouring plies as well [22–26]. Bridging mechanisms increase the toughness as a crack grows, leading to a crack resistance curve (R-curve) [18–21,27]. Materials with rising R-curve behaviour can be characterised by the value at the initiation of the crack propagation [28]. Matsuyamab et al. [29] measured the inter-laminar shear strength of reinforced carbon fibre/carbon matrix composites using a 3-point bending of a short beam and double-notch shear (DNS) testing. DNS testing results in a well-defined single shear failure and leads into a consistent and conservative inter-laminar shear strength. Chiao et al. [30] announced the difficulty in cutting the notches accurately to the prescribed depth of DNS specimens. Shokrieh et al. [31] characterised the inter-laminar shear strength of UD graphite/epoxy under static and fatigue compressive loading and therefore verified the DNS testing, using the proper specimen geometry, as simple and reliable testing method. Inducing pure in-plane shear of a DNS specimen requires a 90°-loading direction, which leads under tensile loading to a tensile matrix failure prior to inter-laminar shear failure. The matrix strength in compression is higher than in tension. Therefore, a compressive loading is suggested. To prevent out-of-plane deformation of the specimen a supporting jig was used. According to ASTM D-3846-08 [32], failure in shear of the DNS specimen occurs between the two notches being machined halfway through the specimen thickness. In contrast to ASTM D-2344, it allows for reliable testing of parallel and non-parallel FRP specimens and is therefore the preferred method.

The focus of the present work is to reach for the limit of inter-laminar properties of FML investigating different Al ply architectures with untreated as well as nanoscale sculptured surfaces. The FMLs are manufactured by the RTM process with two Al plies placed in the mid plane of the composite to investigate the interfacial adhesion between metal and matrix. Two Al plies are used to avoid early debonding at the fibre/matrix interface as occurring for single untreated Al plies placed in the composite mid plane. All laminate configurations are tested by the DNS testing method according to ASTM D-3846-08 [32]. DCB tests according to ASTM D-5528 [33] and ENF tests according to ASTM D-7905 [34] are performed to characterise the inter-laminar fracture toughness of FMLs with nanoscale sculptured metal plies in terms of standard testing methods. The results are demonstrated on the examples of laminates with perforated Al sheets (pre-treated/untreated) as well as in comparison with a standard GFRP laminate. The fracture surfaces are examined by scanning electron microscopy (SEM) and

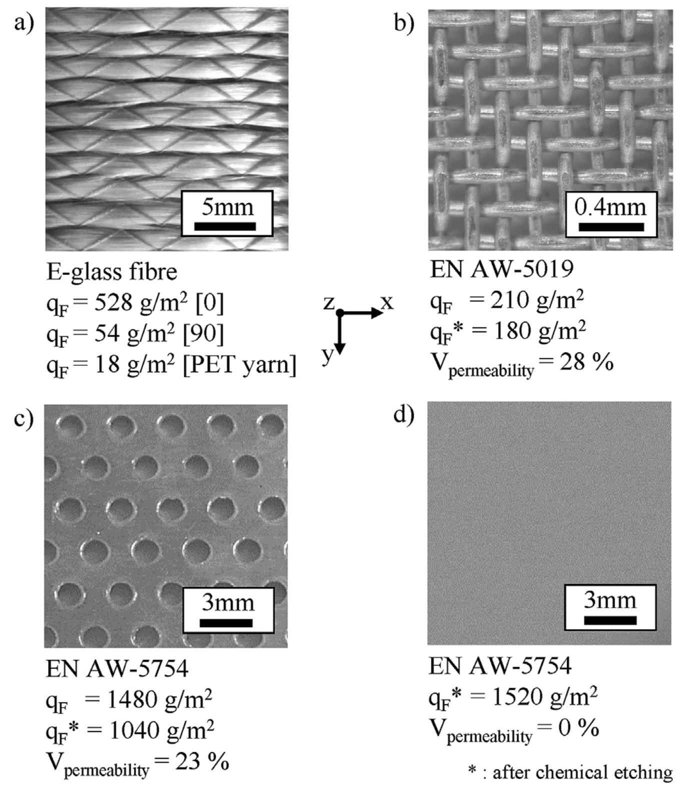


**Fig. 1.** Structure and mass per unit area of the materials: a) glass fibre NCF, b) Al fibre fabric (AA5019), c) perforated Al sheet (AA5754), d) plain Al sheet (AA5754).

optical light microscopy.

## 2. Material and methods

### 2.1. Material

The GFRP composite consists of E-glass fibre (coupling agent silane) non-crimp fabrics (NCF) (mass per unit area ($q_F$) = 528 g/m$^2$ in 0°-direction, $q_F$ = 54 g/m$^2$ in 90°-direction and $q_F$ = 18 g/m$^2$ PES sewing yarn) (R&G Faserverbundwerkstoffe GmbH). For the hybrid composites, Al plies are added. The aluminium plies are cleaned with aceton before being placed in the RTM mould. The permeable metal plies are positioned without specific alignment of the holes/mesh to each other. Additionally, some Al plies undergo the chemical nanoscale sculpturing process being described in detail in section 2.2. Fig. 1 shows the structure and mass per unit area of the materials. For the DCB and ENF specimens, a thin PTFE insert (h = 10 μm) (Goodfellow) is placed in the mid plane of the laminates, which serves as a delamination initiator. Table 1 summarises the lay-up, fibre volume fraction ($V_f$), metal volume fraction ($V_{metal}$) and density (ρ) of all laminates.

For the matrix resin RIMR 135 and hardener RIMH 137 (Momentive Inc.) are used. During the RTM process, the laminates are cured in a mould ($t$ = 5 mm) at 30 °C for 48 h. The specimens are cut and the edges polished with SiC sandpaper. Cutting the notches of the DNS specimens accurately to the prescribed depth is undertaken using a precision cutting machine ATM Brilliant 220. Light microscopy is used to inspect the quality of each specimen visually (Fig. 2). All composites show a high inter- and intra-laminar matrix wetting with no visible imperfections. The permeable Al plies allow the matrix flow through the thickness direction during the injection process, which decreases the injection process time several minutes. After the specimen preparation a post-curing of 15 h at 80 °C is performed to obtain an onset glass transition temperature of $T_{g,onset}$ = 90 ± 1 °C. Furthermore, the