Composites: Part B 69 (2015) 296–303

Contents lists available at ScienceDirect

Composites: Part B

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

Chemical functionalization of composite surfaces for improved structural bonded repairs

Ines Jölly [a], Sandra Schlögl [a,*], Markus Wolfahrt [a,b], Gerald Pinter [c], Martin Fleischmann [b], Wolfgang Kern [a,d]

[a] Polymer Competence Center Leoben GmbH, Roseggerstrasse 12, Leoben 8700, Austria
[b] FACC Operations GmbH, Breitenaich 52, St. Martin Innkreis 4973, Austria
[c] Materials Science and Testing of Plastics, University of Leoben, Otto Glöckel-Strasse 2, Leoben 8700, Austria
[d] Chemistry of Polymeric Materials, University of Leoben, Otto Glöckel-Strasse 2, Leoben 8700, Austria

ARTICLE INFO

Article history:
Received 28 January 2014
Received in revised form 29 August 2014
Accepted 6 October 2014
Available online 19 October 2014

Keywords:
B. Adhesion
B. Fracture toughness
E. Joints
E. Surface treatments
Carbon-fiber reinforced polymers

ABSTRACT

In terms of lightweight design, aerodynamics and structural integrity, bonded repairs represent the preferred approach for repairing composite structures in aircraft applications. In this work the influence of crucial surface parameters including roughness, polarity and chemical composition on the performance of bonded repairs is studied. Besides mechanical and physical interactions, the study aims at the surface modification of carbon-fiber reinforced polymers (CFRP) to tailor chemical interactions with the adhesive. Reactive epoxy and mercapto derivatives are attached onto the CFRP surface by a 2-step functionalization route to ensure optimized adhesion and covalent bonding to epoxy-based adhesives. The performance of bonded coupon joints is determined by single lap shear tests (tensile-shear loading) and fracture mechanical tests (mode I loading). The results give evidence that chemical interactions play a key role in the quality of bonded repair systems. By controlling the chemical surface properties improved bond strength, homogenous crack growth and cohesive failure patterns are achieved.

1. Introduction

Due to their versatile properties, among them high structural efficiency, low weight, enhanced fatigue tolerance and corrosion resistance carbon-fiber composites manufactured in laminate or honeycomb sandwich form are often employed in aircraft designs [1]. However, the brittle nature of CFRP structures makes them susceptible to damage, in particular due to mechanical loads and environmental conditions. It should be noted that failures can occur from the lamina to structural-scale during service. Besides the development of efficient joining technologies, improvement of structural maintenance and prevention of in-service damage, the optimization and development of reliable repair technologies represents a key aspect in current designs of composite structures for aircraft applications [2–4].

Bonded repair techniques provide a common approach to repair structural components if the damage is not extensive as they comprise sufficient aerodynamic performance, good joint properties and improved stress transfer mechanism. In dependence on the type and location of the damage various repair concepts including injection, doubler and scarf-based patches are utilized. In terms of aerodynamically smooth surfaces and permanent restoration of structural strength, scarf repairs offer one of the most promising repair techniques for aircraft applications, particularly for external skin panels [5–7].

When it comes to scarf repairs the damaged material and also a large amount of undamaged material is removed from the structural component by machining process to obtain a scarf cavity with straight or alternatively stepped tapers comprising a shallow angle. The subsequent repair is carried out with either pre-cured patches or processed in-situ with wet-layup or prepreg approaches [8,9]. As mechanically fastened composite repairs suffer from stress concentrations induced by the mechanical fasteners, adhesively bonded repair patches represent the preferred strategy. In terms of adhesively bonded repair patches the adhesion and wettability between the parent material and the repair patches is crucial for good joint performance and high bond strength. Besides joint design, curing and type of adhesive the surface properties strongly govern the joint strength of bonded repairs [5,10–12]. On industrial scale the scarf surfaces are commonly cleaned with organic solvents to remove dust, debris and various surface contaminants.

* Corresponding author. Tel.: +43 3842 402 2354; fax: +43 3842 402 2352.
E-mail address: sandra.schloegl@pccl.at (S. Schlögl).

http://dx.doi.org/10.1016/j.compositesb.2014.10.020
1359-8368/

To ensure a sufficient surface uniformity together with improved surface roughness (in particular for mechanical interlocking) the surfaces are mechanically pretreated (e.g. with abrasion techniques). In addition, plasma- and laser technologies are employed in order to improve the hydrophilicity and wettability of the composite surfaces [6,13]. Although the chemical surface composition and adhesion properties, respectively, can be changed by plasma methods it has to be considered that from the chemical point of view undefined surfaces are achieved that bear a great variety of different oxygen moieties ranging from carbonyl to oxiran groups at their surface [14,15].

The present work aims at the functionalization of CFRP surfaces to obtain composite materials with well-defined surface characteristics including surface polarity, reactivity and wettability. Chemically reactive surfaces are achieved in a two-step approach involving a corona treatment in the first step and a subsequent coupling of functional trialkoxy silanes and thiols via wet chemical methods. The covalent attachment of silanes and thiols onto the surface of either organic or inorganic materials is well established and is not only employed for the preparation of self-assembled monolayers but also widely used in different fields of applications ranging from coating techniques to the health care sector [16–18].

The surface properties of functionalized CFRP materials have been characterized by photo electron spectroscopy (XPS) measurements, wetting experiments with epoxy-based thermosetting resins and contact angle measurements. The results clearly show that the 2-step functionalization ensures the preparation of well-defined CFRP surfaces with reactive anchoring groups including epoxy and mercapto moieties that provide improved adhesion to epoxy-based adhesive patches. The influence of the surface functionalization on the mechanical properties of bonded coupons is determined using lap shear tests and fracture mechanical tests. From the results it can be concluded that the attachment of the selected anchor groups leads to a considerable increase of fracture toughness as well as the tensile lap shear strength which are comparable to the joint performance of mechanically pre-treated (e.g. sanded) CFRP materials. Whilst sanded coupons exhibit inhomogeneous crack growth behavior and partly adhesive failure, surface functionalized bonded coupons entirely comprise cohesive failure patterns with homogeneous crack propagation.

2. Experimental part

2.1. Materials and chemicals

The functional organosilane (3-glycidoxypropyl)-trimethoxysilane (GPTMS) was obtained from ABCR (Karlsruhe, Germany) and the poly-functional thiol pentaerythritol tetra(3-mercaptopropionate) (TetraThiol) was supplied by Bruno Bock Thiochemicals (Marschacht, Germany). All other chemicals were purchased from Sigma–Aldrich (St. Louis, USA) and were used without further purification. The carbon fiber reinforced prepreg material Cycom® 970/T300 was supplied by Cytec Engineered Materials (Wrexham, Great Britain) and comprised an epoxy based thermosetting resin. This prepreg material was used for fabrication of coupon plates with unidirectional layup (60% fiber volume fraction). All laminate plates were autoclave-cured at 177 °C under 6 bar pressure for 2 h. For surface analysis and mechanical testing coupons were cut from the cured plates with a cutting machine (Diadisc 5200, Mutronic Präzisionsgerätebau, Rieden, Germany) comprising a diamond-coated cutting blade. An unsupported epoxy-based resin structural adhesive film with an amine-based hardener and a nominal thickness of 0.24 mm (Scotch-Weld™ AF-163-2U) was employed as adhesive and was purchased from 3 M (St. Paul, USA). In order to prepare the bonded specimens the film adhesive was press-cured at 125 °C for 60 min employing a pressure of 3 bar.

2.2. Sample preparation and surface treatment

Untreated samples as reference were cleaned with isopropanol and dried with compressed carbon dioxide. In terms of abrasive surface treatment, the coupons were sanded with a SiC-sanding paper comprising a grit number of 150. The grit size of the angular grinder was chosen in compliance with previous reports that state that a grit number in the range of 100 is appropriate for abrasive pretreatment procedures in composite repairs [19]. After sanding the samples were cleaned with isopropanol and dried with compressed carbon dioxide. For the contact angle measurements the sanded samples were polished with a polishing machine (Buehler, USA) using a diamond solution with a particle diameter of 3 μm. The polishing was carried out to avoid any surface roughness effects during contact angle measurement.

The chemical surface functionalization of the coupons was carried out with a 2-step procedure. In the first step the coupon surface was oxidized by an atmospheric pressure-plasma treatment (laboratory corona station PG 3001, Ahlbrandt System, Lauterbach, Germany). Without any delay the corona treated coupons were immersed in GPTMS and TetraThiol, respectively. After 12 h at room temperature the coupons were removed from the solutions, rinsed with tetrahydrofuran for three times and dried in an oven at 60 °C for 30 min.

2.3. Characterization of the composite surfaces

Wetting experiments were carried out with an epoxy-based thermosetting resin comprising 49.99 wt.% diglycidyl ether of bisphenol A (DGEBA), 49.99 wt.% 2-methylhexahydrophthalic anhydride and 0.02 wt.% dimethyl benzyl amine as accelerator. A thin resin layer (90 μm) was applied on the untreated and modified coupon surfaces and after a thermal curing step at 155 °C for 10 h the morphology and wetting characteristics of the cured resin were characterized by optical techniques.

Contact angle measurements were performed by using a drop shape analysis system, DSA 100, from Krüss GmbH, (Hamburg, Germany). De-ionized water and diiodomethane were used as test liquids and the surface energy was estimated according to Owens and Wendt, Rabel [20,21]. The static water contact angles were measured before and after modification.

XPS analysis of pristine and functionalized coupon surfaces were performed with a K-Alpha photoelectron spectrometer (Thermo Fisher Scientific, Waltham, USA) equipped with an Al Kα X-ray source ($h\nu$ = 1468.6 eV). The lateral resolution was 30 μm and the energy resolution amounted to 0.5 eV. The topology of the abrasive treated surfaces and the fracture patterns were further evaluated by confocal (Micro Prof MPR 1080, Fries Research & Technology GmbH, Bergisch-Gladbach, Germany) and scanning electron microscopy (Zeiss DSM 962, Carl Zeiss MicroImaging, Germany).

2.4. Quasi-static mechanical testing

Single lap shear coupons were manufactured according to ASTM D5868-01(2008) [22]. Doubler tabs were bonded to the ends of the lap shear coupons to establish a centric load application. For the fracture tests under mode I loading conditions double cantilever beam (DCB) specimens, as shown in Fig. 1, were prepared according to Blackman and Kinloch [23]. The test protocol published by the authors is a development of the ASTM Standard D3433 [24] and offers a corrected bean theory calculation method (CBT method). This method incorporates several extra corrections which