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Interfacial shear strength studies of experimental carbon fibres, novel thermosetting polyurethane and epoxy matrices and bespoke sizing agents

Florian Gnädinger [a], [*], Peter Middendorf [a], Bronwyn Fox [b]

[a] Institute of Aircraft Design, University of Stuttgart, Pfaffenwaldring 31, Stuttgart, 70569, Germany
[b] Faculty of Science, Engineering and Technology, Swinburne University of Technology, Hawthorn, VIC 3122, Australia

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ABSTRACT

The strength and nature of the fibre-matrix connection affects many of the key mechanical characteristics of composite parts. The complex interplay of fibre surface, sizing agent and matrix material has been a longstanding problem and receives substantial attention when new ingredients are introduced. For the first time, this study investigated a novel thermosetting polyurethane resin together with a set of experimental carbon fibres. The fibres were manufactured using a unique facility that closely models a commercial production line. This equipment allowed extracting fibres after carbonisation, after electrochemical surface treatment and after coating with epoxy, polyurethane and polyamide based sizing agents. A commercial carbon fibre and a state of the art epoxy resin were selected as reference materials. The single fibre fragmentation test was used to measure the interfacial shear strength (IFSS) of the resulting combinations. The results show the enormous importance of etching away the relatively inert outer layer during surface treatment as the IFSS increased by factor 2.6. The newly developed polyurethane resin showed for unsized fibres up to 50% higher values for the IFSS than corresponding combinations employing epoxy resin. This superiority melted down to 5–21% when looking at the sized fibres, showing the need for developing sizing agents that facilitate adhesion to polyurethane matrices. A relative advantage of identical sizing and matrix polymer could be found when looking at sized fibres. Photoelastic investigations of the fragmented specimens supported the measured values for the IFSS. There was a close correlation between high IFSS results and strong photoelastic stress patterns.

1. Introduction

Carbon fibre reinforced plastics are a synergistic combination of 2 material classes that exhibit completely different properties regarding strength, stiffness, shape, media and temperature resistance. The strength and nature of the fibre-matrix connection affects many of the key mechanical characteristics of composite parts, in particular off-axis tension and flexure, shear and dynamic strength as well as damage tolerance and energy absorption [1–3]. Although many previous studies have focussed on investigating the interphase region between fibre surface and bulk matrix, we are still no closer to developing an understanding of how this important interaction can be tailored to optimise adhesion [4]. Recent work has explored fibre surface modification by electrochemical treatment, plasma or by the addition of carbon nanotubes/nanoparticles in order to activate the relatively inert surface after carbonisation and thereby improve adhesion [5–7].

In commercial carbon fibre production, after electrolytic surface treatment, the fibres usually are coated with a thin layer of polymer sizing to facilitate handling and protecting the fibre during weaving and textile processes by realising strand integrity and protect the individual filaments [8–10]. This additional component strongly affects not only fibre-matrix adhesion, but also can change other parameters like brittleness of the composite [1,2]. Common sizing polymers for thermoset resins are based on off-stoichiometric epoxy or polyurethane resins. While epoxy is also a widespread bulk matrix material, thermosetting polyurethane matrix systems are relatively new developments. They are becoming increasingly commercially important due to their ability to achieve short cure

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[*] Corresponding author.
E-mail addresses: florian.gnaedinger@ifb.uni-stuttgart.de (F. Gnädinger), peter.middendorf@ifb.uni-stuttgart.de (P. Middendorf), blfox@swin.edu.au (B. Fox).

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cycle times. Viscosities of 50–200 mPa s allow fast wetting of fibres and the released cure reaction heat is around 50% below comparable epoxy systems. A decreased likelihood of undesirable localised exotherms makes this new generation of polyurethanes suitable for the production of thick laminates (>5 mm). Further advantages of polyurethane matrices are properties such as their high intrinsic toughness, fatigue and damage tolerance [11–13].

Evaluating the quality of fibre-matrix adhesion can be done in different ways [3]. A straightforward approach is measuring interface-sensitive laminate values like off-axis tension and flexure or in-plane shear strength [14]. A major problem is the ambiguous influence of the investigated parameters, e.g. when different sizings also affect processing and therefore laminate quality. This drawback motivates an isolated examination of single filaments embedded in a bulk matrix, e.g. the single fibre fragmentation test (SFFT), microindentation techniques and the fibre pull-out and microbond technique [3]. Furthermore, fibre surface analysis with scanning probe or scanning electron microscopy (SPM and SEM) or X-ray photoelectron spectroscopy can support the investigation [15].

The SFFT is used for examining fibre-matrix adhesion in composites using 6 different fibre types and 2 different thermosetting resins. *Henkel Loctite Max* is a novel thermosetting polyurethane resin that is currently under development aiming at automotive and wind energy applications. *Sika Biresin CR131* with *CH135-4* hardener is a commercial epoxy resin aiming at applications with demand for increased temperature resistance, e.g. small aircrafts and tanks.

The fibres were manufactured using a unique facility that closely models a commercial production line, referred to as a “single tow fibre line” and coated with epoxy, polyurethane and polyamide based sizing polymers. The selection of sizing agents allowed to investigate, if there is a positive effect on fibre-matrix adhesion when matrix and sizing polymers are based on the same chemistry. Polyurethane sized fibres, embedded in polyurethane resin and the epoxy sized fibres, embedded in epoxy resin were compared to unequal combinations. Next to that, unsized fibres (electrochemically untreated and treated) as well as commercial fibres from *Toho Tenax* were investigated. These additional fibres allowed to benchmark the effects of coating and the quality of the experimental in-house fibres.

2. Material and methods

2.1. Material

2.1.1. Fibre and sizing material

Experimental carbon fibres were manufactured from *BlueStar 0.77dTex 24k* polyacrylonitrile precursor. The fibres were carbonised, surface treated and sized using a scale model of a commercial carbon fibre line (single tow fibre line) designed and developed by *Despatch Industries* (Minneapolis, United States). The single tow fibre line consisting of stabilization ovens, carbonisation furnaces and surface treatment and sizing baths enabled precise control of fibre temperature, tension and residence time in addition to control of all parameters involved in fibre electrolytic treatment and sizing. The access to this equipment allowed in-line fibre treatment, making the results representative of a commercial process and decreasing the likelihood of contaminating the fibres. In contrast to that, most former studies have relied on de-sizing the fibres and doing post-processing treatment.

Carbon fibres without surface treatment and sizing were collected directly after the high temperature furnace which was set to 1400 °C. Fibres with surface treatment but without sizing were collected after they had been running through an electrolytic bath with 12 V and 3.2 A. Next, they ran through a 1:10 solution of sizing polymer and water. 3 different sizing agents that were provided by *Michelman* (Cincinnati, United States), have been investigated within this study. *Hydrosize® EP834* is a partially cured epoxy resin delivered as a non-ionic epoxy dispersion [16]. It was used to produce *experimental EP-sized fibres* with a sizing content of 1.7%. The sizing bath was exchanged and using *Hydrosize® U6-01*, a water-based polyurethane solution, *experimental PU-sized fibres* with a sizing content of 1.0% were produced [17]. The wetted *EP-* and *PU-fibres* ran through a squeezing wheel and were dried in a vertical radiation oven at 140–160 °C for 3 min. The third sizing agent was *Hydrosize® PA845H*, a polyamide dispersion with a melting point of 160 °C [18]. Therefore, the radiation oven was set to 180–200 °C in order to ensure melting of the sizing on the fibre surface. The *experimental PA-sized fibres* had a sizing content of 0.9%.

Furthermore, the polyurethane coated 24 k carbon fibre *STS40 F13 24k 1600tex* from *Toho Tenax* with a sizing content of 1.0% served as a commercial reference to these experimental in-house fibres [19].

The sizing content was measured according to DIN EN ISO 10548. The polyurethane and epoxy based sizing agents were dissolved with acetone and the polyamide based sizing agent with a 30% hydrogen peroxide solution. SEM micrographs of de-sized fibres were used to confirm that de-sizing had taken place.

2.1.2. Matrix material

This study investigates a novel and proprietary thermosetting polyurethane resin developed by *Henkel AG & Co. KGaA* (Düsseldorf, Germany). Similar to the processing of thermosetting epoxies, part A (based on polyether polyols) and part B (based on aromatic derivatives of methylene diphenyl diisocyanate (MDI)) were mixed in stoichiometric quantities. The fabrication of polyurethane resin specimens required some modifications in comparison to conventional epoxy resin because the presence of moisture led to bubbles within the specimens:

1. Conventional silicone moulds were found to lead to bubbles within the PU-specimens during post-curing. Polypropylene moulds are recommended.
2. Degassing and drying the polyol and isocyanate components prior to mixing at 70 °C was found to decrease the moisture content.
3. Mixing the components for 7–8 min is recommended in order to reach the clearing point. Otherwise, the components may separate again before curing is completed.
4. When mixing is not done with a vacuum speed mixer, degassing at 30 mBar is recommended before pouring the resin into the moulds.
5. It was very important that the polyurethane resin cured at 90 °C to realise a high degree of cross-linking at this first curing stage. Otherwise, bubbles would occur during post-curing and could not exit the solidified specimens.
6. For compressing potential bubbles to a harmless size, it is recommended that curing takes place in a pressurised environment, e.g. in a pressure pot with 7 bar overpressure.

The thermosetting polyurethane was evaluated and compared to a state of the art thermosetting epoxy resin *Sika Biresin CR131* (based on 50–100% bisphenol A diglycidyl ether (DGEBA), 10–20% bisphenol F diglycidyl ether (DGEBF) and 5–10% 1,4-bis(2,3-epoxypropoxy)butane) with *CH135-4* hardener (based on triethyleneteramine (TETA)). Both matrix materials are comparable in terms of mechanical and physical properties (Table 1).