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The influence of a thermoplastic toughening interlayer and hydrothermal conditioning on the Mode-II interlaminar fracture toughness of Carbon/Benzoxazine composites

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ABSTRACT

Carbon fibre/Benzoxazine laminates with and without non-woven polyamide (PA) fibre veils at the interlaminar regions were manufactured using vacuum assisted resin transfer moulding (VARTM). The effect of the interlaminar thermoplastic veils on the Mode-II critical strain energy release rate (G_{IIC}), under both wet and dry conditions, was determined using two commercially available Benzoxazine resins: a toughened system and an untoughened system. In all samples the toughened system outperformed the untoughened system. The overall resistance to Mode-II crack growth was significantly improved by the inclusion of the interlaminar veils due to an increase in the thickness of the matrix-rich interlaminar region, plastic deformation of the PA fibres and a crack-pinning mechanism. Moisture caused an increase in matrix ductility, which improved the resistance to crack initiation; however, this was counteracted by a reduction in fibre/matrix interfacial strength causing a reduction in resistance to crack growth.

1. Introduction

Composite materials are a popular choice for high-performance applications – such as aerospace structures – as they provide high specific stiffness and strength and corrosion resistance. The ever-increasing popularity of composite materials has meant that there is a greater interest in the development and use of advanced, low-cost fabrication methods – primarily resin infusion techniques, such as resin transfer moulding (RTM) and vacuum assisted resin transfer moulding (VARTM) – to manufacture large, complex and high-quality composite parts in medium-volume quantities using low-cost tooling. These types of processes have the ability to reduce costs through single-step manufacture of the material and part and also by manufacturing integrated parts (e.g. skin panels with integrated stiffeners and stringers). Thermosetting polymers are suitable for use in infusion manufacturing techniques as they provide good mechanical properties and chemical resistance at a low cost, as well as having lower viscosities and processing temperatures than thermoplastic matrices. However, highly crosslinked thermosetting polymer matrices are inherently brittle and can have relatively poor fatigue performance, leading to a high susceptibility to damage from out-of-plane loading (e.g. due to impact events) and this can potentially limit the use of the materials in certain primary aircraft structures.

High damage tolerance is a key requirement for composite materials used in aircraft structures; hence a high resistance to delamination is essential. The interlaminar properties of laminated composite structures depend solely on the characteristics of the matrix and interface, and represent a major source of weakness under conditions that generate shear stresses [1]. The high level of interlaminar shear stresses generated during an impact event indicates the importance of the Mode-II critical strain energy release rate (G_{IIC}) – which will be referred to as the Mode-II interlaminar fracture toughness (ILFT) for the purposes of this paper – in improving impact resistance. Unfortunately, resin materials with high toughness are often associated with high viscosity, which is problematic for infusion manufacturing techniques. Therefore, delamination resistance of infused thermosetting composite laminates can often be far below the requirements due to inadequate performance of the matrix-dominated interlaminar region [2].

Several strategies have been employed to improve the overall ILFT and subsequent impact performance of composite laminates. For example, the use of fabric architectures, such as woven [3–6], 3D woven [7], knitted [8], braided [9,10] and spread-tow

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[11–13], have proven to enhance the damage tolerance of composite laminates. Through-thickness reinforcements, such as Z-pinning and stitching, have also been successful in increasing the impact resistance of laminates; however, they have been shown to decrease in-plane properties due to crimping of the fibres and by causing stress concentrations at the pins or stitches [14,15].

Standard methods for enhancing toughness in carbon fibre composites by modification of the constituents follow two approaches: toughening of the bulk resin and toughening of the weak interlaminar region. A review on the use of thermoplastic and rubber modifiers to enhance the toughness of thermosetting matrix composites can be found in Ref. [16]. Much research has been dedicated to improving the fracture toughness of thermosetting resins used in the manufacture of composite laminates through the use of liquid rubber toughening [17–21], thermoplastic polymer blends [22–27], core–shell particles [28–32] and hyper-branched polymers [33–36]. These toughening techniques work on the general principle that the toughener is initially soluble in the matrix resin; the modified resin is infused into the dry preform, and during the curing reaction the mixture undergoes phase separation to form a toughened morphology within the matrix. However, as toughened resins can often be too viscous for use in infusion techniques, another method of resin modification is required. One promising technique involves incorporating in the preform a thermoplastic toughener that is soluble in the resin-matrix. The unmodified resin is infused into the preform, dissolves the thermoplastic toughener and phase separates during the curing reaction to form a toughened morphology. The toughener can be in the form of thermoplastic electrospun nano-fibres at the interlaminar regions [37–41], or thermoplastic fibres that are co-woven into the reinforcing fabric (e.g. PRIFORM® (Cytec)). However, in the case of interlaminar nano-fibres, it has been observed that thick interlayers may actually reduce the interlaminar properties due to an increased number of voids [42].

New resin chemistries have been developed to address the need for improved performance, while also catering to the requirement for reducing costs associated with manufacture. Henkel Corporation has developed a range of Benzoxazine resins for structural aerospace applications. The development objectives were to provide the aerospace industry with a resin technology to bridge the gap in performance between high performance epoxy of 140 °C hot/wet T_g and BMI of 220 °C hot/wet T_g [43]. Benzoxazine resin systems can have over 2.5 times the toughness, high modulus and low moisture absorption compared to unmodified epoxies, and it has previously been shown to outperform other comparable resin systems as a composite matrix [44]. The resin can also be stored at ambient temperatures, which is an additional attraction.

The second popular method for enhancing the toughness of composite laminates is interleaving, whereby a tough interlayer is used to enhance the impact resistance of the weak interlaminar region. Thermoplastic interlaminar particles have proven to be extremely effective for prepreg materials – the Boeing 787 fuselage, for example, is manufactured from a carbon fibre/epoxy prepreg tape T800H/3900-2, whose interface contains a discrete thin layer of toughened thermoplastic particles, which has exhibited very high impact damage resistance [45]. Thermoplastic films have also been shown to improve the ILFT of prepreg laminates [46,47], but can inhibit the through-thickness percolation of the resin in infusion methods. Non-woven fibre veils have proven to be successful in improving Mode-I and -II ILFT as well as impact properties of composite laminates [48–51]. They represent an economical and efficient method of toughening with the potential for use as distribution media in thick laminates [52], as tougheners for the bondline in composite repairs [53,54] and as a method for improving conductivity [45].

Hygrothermal environmental conditions are a serious concern for fibre-reinforced polymers (FRP) as the fibre/matrix interface often provides a route through the material for small water molecules. In studies of moisture effects, it is generally observed G_{IIC} decreases with moisture content in carbon/epoxy composites [55–58]. Todo and Nakamura [55] conducted an investigation into the effect of moisture on the Mode-II static and dynamic response of carbon fibre/epoxy laminates. They used two different types of prepreg to manufacture laminates – one with epoxy cured at 120 °C and another with a thermoplastic-modified epoxy cured at 180 °C. It was found that the carbon/toughened epoxy laminate had a higher percentage moisture uptake than the standard carbon/epoxy, and also exhibited different failure mechanisms. Hence, it is important to quantify the moisture uptake and subsequent mechanical behaviour of thermosetting composite laminates toughened by a thermoplastic inclusion.

Mode-I delamination has been studied extensively in relation to toughened laminates, as described in Refs. [46,48,51,59,60] for example. The work presented in this paper is a continuation of a previous investigation conducted by the authors into the improvements achieved in Mode-I ILFT and flexural properties of Carbon/Benzoxazine laminates interleaved with a non-woven PA fibre veil [51]. The primary objective of the current investigation is to determine the effectiveness of non-woven PA veils in improving the resistance of Carbon/Benzoxazine laminates to Mode-II fracture, as this is a prevalent fracture mechanism in impact damage. The End Notched Flexure (ENF) three-point bend test method will be used to measure G_{IIC}. A toughened (BZ9120) and an untoughened (BZ9130) Benzoxazine matrix system are used in this study. Furthermore, the effect of moisture on the Mode-II ILFT of baseline and toughened laminates for both matrices was investigated.

2. Experimental

2.1. Materials

Carbon fibre laminates were manufactured using 0°/90° Non-Crimp Fabric (NCF), with an areal weight of 559 g/m^2, based on high tensile strength carbon fibres (TENAX® E HTS40 F13 12K 800tex) supplied by Saertex GmbH (Germany). The fabric is made up of a layer of 0° fibres on top of a layer of 90° fibres bound together using an epoxy powder binder (Cytec CYCOM 7720 RTM) and stitched using PES 48 dtex in a tricot warp pattern. The resins are commercially available Benzoxazine resins developed specifically for use in liquid composite moulding technologies – Loctite® BZ9120 AERO and Loctite® BZ9130 AERO – supplied by Henkel AG & Co. KGaA (Germany). BZ9120 is a toughened Benzoxazine resin designed to meet aerospace damage tolerance and temperature requirements and BZ9130 is a Benzoxazine resin for high temperature applications [61]. Details on the physical and

Table 1
Physical and mechanical properties of the two Benzoxazine resin systems used in this study[a].

Property	Loctite® BZ9120 AERO	Loctite® BZ9130 AERO
Cure temperature (°C)	180	185
Cure time (min)	90	120
Post-cure	None	232 °C/60 min
Heat of cure DSC (J/g)	300	276
Density (g/cm^3)	1.21	1.20
T_g (dry/wet °C)	183/148	253/192
Flexural strength (MPa)	146	100
Flexural modulus (GPa)	3.5	3.5
Resin fracture toughness, G_{IC} (J/m^2)	472	352

[a] Source: Li et al. [61].