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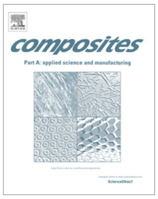

The influence of hydrothermal conditioning on the Mode-I, thermal and flexural properties of Carbon/Benzoxazine composites with a thermoplastic toughening interlayer

N.H. Nash, D. Ray, T.M. Young, W.F. Stanley *

Irish Centre for Composites Research (IComp), Materials and Surface Science Institute (MSSI), University of Limerick, Castletroy, Co. Limerick, Ireland

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ABSTRACT

Carbon/Benzoxazine laminates with and without non-woven thermoplastic fibrous polyamide (PA) veils at the interlaminar regions were manufactured using Vacuum Assisted Resin Transfer Moulding (VARTM). The effect of the interlaminar thermoplastic veils on the Mode-I strain energy release rate (G_{IC}), flexural stiffness, glass transition temperature (T_g) and water absorption behaviour was determined using two commercially available Benzoxazine resins. Despite an increase in the maximum moisture content, the veils greatly enhanced G_{IC} by an increase in fibre bridging of PA fibres, with concurrent reductions in flexural stiffness. Water ingress resulted in large reductions in the T_g, although no significant change was observed due to the PA interlayers. Fibre bridging and fibre pull-out were the main mechanisms by which the veils assisted in resisting delamination. The presence of the water was observed to degrade mechanical properties due to a reduction in fibre/matrix interfacial strength, molecular degradation and plasticisation of the matrix.

1. Background

Composite materials are used increasingly in the aircraft, automotive, marine and wind energy industries as they boast high specific strength and stiffness. Out-of-autoclave (OOA) manufacturing processes – such as the Vacuum Assisted Resin Transfer Moulding (VARTM) process – have become increasingly popular in recent years as a method to reduce the cost of manufacture of high performance composite components. Due to processing considerations (e.g. viscosity, processing temperatures, etc.), these processes almost exclusively use thermoset resins that are relatively brittle and result in a composite laminate that is susceptible to impact damage (e.g. matrix cracking, fibre/matrix debonding and delamination). This may limit the use of thermosetting composites in structural applications as the damage generated is often difficult to detect and can considerably reduce mechanical performance [1]. It has been shown that this susceptibility is a limiting factor in the application of composite materials. The strength of composite structures drops significantly after sustaining an impact because the loaded fibres are fractured (high velocity impacts) or have debonded from the matrix causing delaminations (low velocity impacts) [2]. Delamination is recognised as perhaps the most critical damage process in laminated composites. In an impact situation, delaminations are caused by the high shear stresses generated due to bending of the laminate (i.e. Mode-II loading). However, most real-life composite structures will generally be subjected to Mixed-Mode loading conditions [3]. Delamination resistance can, however, be improved by manufacturing a three-phase composite: fibre, matrix, toughener [4]. Hence, the improvement and tailoring of composite properties for out-of-plane loading has become an important research topic. Delaminations generally propagate through crack-shearing (Mode-II) during an impact event and through crack-opening (Mode-I) during compressive loading of the structure; therefore, much research has focused on toughening additives and their effect on Mode-I and -II fracture resistance.

The Achilles' heel of thermosetting resins is toughness, and hence much work has been dedicated to bulk matrix toughening. Studies have shown that toughening the bulk matrix system with particles – such as thermoplastics [4–6], carbon nanotubes [7,8] and rubber [9] – can enhance the Mode-I fracture toughness and fatigue performance [10,11] of the composite but can adversely affect other mechanical and thermal properties [12–15]. While it is an effective toughening technique, resin modification tends to increase viscosity – which poses a problem for infusion processing methods, such as VARTM – and particulate inclusions can agglomerate or migrate during resin infusion.

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* Corresponding author. Tel.: +353 61 213505.
E-mail address: walter.stanley@ul.ie (W.F. Stanley).

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Many studies on the use of a toughening phase to enhance the impact and delamination resistance of laminated composites have investigated the use of interlaminar toughening methods (e.g. interlaminar films, particles, fibre veils and electrospun nano-fibres) to reinforce the most delamination-prone areas. Interleaving thermoplastic films have been found to produce significant improvements in G_{IC} (increases of up to double the initial value) and impact properties of prepreg laminates [16–23]. However, they can inhibit resin percolation in the preform thickness direction and are therefore problematic for infusion methods. Particulate modified interlayers are, again, not suited to infusion techniques as particles can migrate and agglomerate due to resin flow. This method has proven to be extremely effective for prepreg materials and is now an industrially accepted toughening method – the Boeing 787 fuselage, for example, is manufactured from a carbon/epoxy prepreg tape with thermoplastic particles located at the interlaminar regions [24]. Tackifiers and binders are often used to increase the handleability of preforms for infusion but can also be used to increase the toughness properties of the final laminate. These are often soluble in the composite matrix and, therefore during infusion, have the potential to migrate, resulting in a non-uniform distribution of the toughener and hence a variance of material properties throughout the laminate [25]. Electrospun thermoplastic nano-fibre mats, which subsequently dissolve and form toughening precipitates in the matrix during curing, has proven to be highly effective in increasing delamination resistance without affecting other material properties or final part geometry [24,26–28]. This is a time-consuming and costly process, which is not yet easily incorporated into a manufacturing process, but it also has the potential to incorporate other components such as carbon nano-tubes (CNT) or core–shell rubber (CSR) particles in order to tailor the properties of the interlayer [29,30]. A recent study by Saghafi et al. [31] found that the inclusion of polycaprolactone (PCL) electrospun nano-fibres at the interlaminar regions of glass fibre/epoxy prepreg laminates enhanced G_{IC} (G_{ICinit} increased by 12% and G_{ICprop} is increased by 17%). This increase was attributed to the dissolution of the PCL fibres in the epoxy matrix and phase-separating during the curing reaction to form a heterogeneous morphology in which a spherical PCL-rich phase was distributed in a continuous epoxy phase. The spherical particles increased the energy absorbed during fracture and hence, increased the Mode-I fracture toughness, The ability of electrospun thermoplastic nano-fibres to dissolve in the matrix and separate during the curing reaction to form a toughening phase has potential for use in infusion manufacturing methods as they act to toughen the matrix after infusion; thereby avoiding the increase in viscosity that would have occurred if the toughener was added prior to infusion.

Published results show that interlaminar thermoplastic fibre veils have the potential to be incorporated easily into Liquid Resin Infusion (LRI) manufacturing processes (e.g. VARTM and Resin Transfer Moulding (RTM)) to manufacture low-cost composites with superior Mode-I properties as they do not involve modification of the resin and therefore do not increase the viscosity of the resin [1,27,32,33]. Peijs and Venderbosch [34] were the first to conduct an investigation into this type of toughening method for carbon and high-performance polyethylene (HP-PE) composites. They observed that the hybrid effect tends to significantly increase the crack propagation energy. Hogg [35] has reported significant improvements in G_{IC} of vacuum infused carbon/epoxy laminates interleaved with different thermoplastic veils. The increase in resistance to delamination propagation was due to increased fibre bridging. Wong et al. [36] used a thermoplastic fibre veil to modify carbon/epoxy laminates manufactured using VARTM. The fibres had the ability to dissolve in the epoxy matrix during cure and phase separate to form a toughening phase along the interlaminar region of the composite. This phenomenon led to a tenfold increase in G_{IC} without affecting the T_g or flexural strength. Kuwata and Hogg [32] conducted an important, in-depth investigation into the Mode-I fracture toughness of carbon/epoxy and carbon/vinyl ester laminates with different fabric architectures manufactured using VARTM and toughened with different combinations of thermoplastic and carbon fibre veils. Similar to previous results, the thermoplastic fibre veils generated much higher G_{IC} values than the hybrid and carbon fibre veils. This was attributed to increased fibre bridging and the ability of the thermoplastic fibres to absorb energy during crack growth as a result of plastic deformation in the fibres themselves.

The applications of this toughening method were highlighted when Tzetzis and Hogg [37] proposed the use of fibre veils to toughen the bond-line of infused repairs. Polyester and carbon fibre hybrid veils were used in the investigation of Mode-I fracture toughness of repaired carbon/epoxy prepreg repairs. Repairs without veils at the bond-line can lead to intermittent crack propagation and interfacial failures without significant dissipation of energy. The incorporation of veils produced a significant increase in G_{IC} due to the strong bond between the epoxy resin and the toughening fibres, substantially increasing the level of fibre bridging.

While the improvements in G_{IC} are well documented, the effects of incorporating an interlaminar thermoplastic non-woven veil on other material characteristics – such as stiffness, thermal properties (e.g. T_g) and water absorption behaviour – have not been investigated in depth. Also, due to the use of composite materials in a variety of applications, the properties of toughened laminates should be characterised over a wide range of environmental conditions [38]. The thermoplastic material that will be used in the non-woven interlaminar veils for this research is PA, which readily absorbs moisture. Hence, it is of vital importance to characterise the impact that this will have on the water absorption behaviour and subsequent mechanical performance of the laminate. Miri et al. [39] observed that the tensile properties of PA 6 films were reduced in the presence of moisture. This was attributed to a modification of chain mobility in the amorphous phase via water plasticisation. It was found that the material was plasticised due to the humidity – by reducing the entanglement and bonding between molecular chains – and hence reduced the mechanical properties and T_g significantly.

Water absorption in composite materials generally results in degradation of a polymeric material and a deterioration of mechanical properties due to the ability of the water molecules to form hydrogen bonds with the polymer chains, essentially attacking the chain [40–44]. However, G_{IC} has been reported to improve under hot/wet conditions [38,45,46]. This is brought about by a reduction in interfacial bonding strength between the fibre and matrix and an increase in ductility of the matrix hence allowing fibre/matrix debonding failure to occur earlier. The reduction in the strength of the interface improves G_{IC} as it facilitates fibre pull-out and fibre bridging.

Relatively little work has been carried out investigating the effect of toughening additives on the rate of moisture ingress in composite materials. Davidson et al. [38] performed tests on both dry and moisture-saturated, carbon/epoxy, prepreg laminates with a thermoplastic particulate toughened interlayer at different temperatures. This study compared the properties of dry and wet toughened laminates; there was no comparison between toughened and baseline laminates. It was observed that the T_g dropped by 19% when samples were moisture saturated. Matrix ductility was observed to increase with increasing temperature and moisture content. There was also a rise in G_{IC} with temperature and moisture content, which was correlated to the associated increase in matrix ductility and its increasing ability to absorb (Mode-I)