Localized toughening of carbon/epoxy laminates using dissolvable thermoplastic interleaves and electrospun fibres

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ABSTRACT

Mode-I interlaminar toughness improvement through epoxy-dissolvable thermoplastic phenoxy interleaves of different surface-to-volume ratios is reported. Shear yielding around the crack tip in the reaction-induced phase separated blend morphology was found to be the main toughening mechanism responsible. The dissolution behaviour of thermoplastic phenoxy fibre within epoxy resin was studied, and a simple relationship between dissolution time, temperature, and original fibre diameter is proposed. Thermoplastic interleaves in the form of continuous films and electrospun fibre mats of equivalent weights were employed in order to study the effect of surface-to-volume ratio on dissolution and toughening behaviour. The toughness improvements obtained for the dissolvable thermoplastic nanofibre interleaves were the highest ever reported for these types of toughening concepts, with a dramatic increment from 0.56 kJ/m^2 to 1.90 kJ/m^2 with only 1.6 wt.% phenoxy interleaves. Differences in toughening behaviour between continuous films and nanofibre mats are explained in relation to differences in dissolution time.

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1. Introduction

The laminated nature as well as intrinsic brittleness of highly cross-linked epoxy matrices limits the out-of-plane fracture toughness of carbon fibre reinforced plastics (CFRP), challenging researcher for many years to develop toughening concepts that increase the resistance to delamination of composite laminates.

Various toughening routes have been studied over the years, with the blending of epoxy resins with low-molecular weight rubbers that phase separate during curing into epoxy–rubber blends being one of the most widespread [1–6]. Although this toughening method has been adapted into numerous industrial applications, the associated drawbacks such as a lowering of the glass transition temperature (T_g), decrease in yield stress, Young's modulus, and thermal and environmental stability have limited this approach to certain less critical applications.

In order to avoid some of the limitations of rubber toughening for highly crosslinked epoxy resins, relatively high T_g thermoplastics have been widely used as an alternative to rubber to improve the fracture toughness of epoxy resins since the late 1980s [7–12].

Various thermoplastics have been introduced into epoxy matrices as toughening agent, including polyether sulfone (PES) [13–15], polyether imide (PEI) [16], polysulfone (PSF) [17], polyphenylene oxide (PPO) [7], polyphenylene ether (PPE) [18,19], polyethylene terephthalate (PET) [19], and polyhydroxy ether bisphenol A (phenoxy) [20–23]. Similar to liquid rubber toughening initially a homogeneous blend is created in these systems, with the epoxy acting as a solvent for the thermoplastic, which phase separates upon curing. Starting reactant mixtures are completely miscible and composed of epoxy monomer, thermoplastic and curing agents. An increase in epoxy molecular weight upon curing leads to reaction induced phase separation and an epoxy/thermoplastic blend, having a two-phase morphology with improved ductility and toughness without significant loss of other mechanical and thermal properties such as modulus, tensile strength and thermal resistance. Many factors are believed to affect the toughening of epoxy matrices, including morphology, end-groups of thermoplastics, crosslink density, etc. [8]. Although the effect of end-group functionalization remains controversial [8,13,24–26], a co-continuous phase morphology, and higher crosslink density are generally regarded as more favourable for optimized toughening without sacrificing other properties. For more detailed reading about the subject the reader is referred to several reviews on the topic [7,8,11,27].

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Localized interlaminar toughening in composite laminates can be achieved through interleaving [4]. Interleaving, involves the inserting of ductile interlaminar layers into composite laminates to enhance the damage tolerance of brittle epoxy based composites. Initially thermoset systems such as carboxyl-terminated butadiene acrylonitrile (CTBN) modified epoxy resins were used as interleaves [28], but also thermoplastics miscible with epoxy resins have been used as interleaves, which can be based on various forms such as film [29], microfibres [30], or electrospun nanofibres [31,32]. Apart from localized interlaminar toughening, another advantage of interleaving over bulk miscible thermoplastic/thermoset blends is related to processability during subsequent composite manufacturing. In the case of miscible blend systems, the high molecular weight thermoplastic will normally lead to an increase in system viscosity and hence interfere with liquid moulding processes such as resin infusion or resin transfer moulding.

Different toughening mechanisms are involved, including plastic deformation and crack bridging, depending on the interleaf form. Various thermoplastics have been employed as interleaved and promising toughening results were obtained for some systems [21,23,30,33–35]. Dzenis and Renekar patented the use of electrospun nanofibre mats as interleaves for toughening already in 2001 [36], while several research works on this topic have been performed since then [31,32,35,37–40]. However, until now limited comparative studies [41,42] have focused on the effect of the interleaf form (i.e. continuous film, non-woven microfibre mat, or electrospun nanofibre mat) on final toughening results.

To the best of authors' knowledge, no study has addressed this issue for the phenoxy/epoxy system, although the type of interleaf is very important in the case of dissolvable thermoplastics as different interleaf forms will show different dissolution behaviour due to differences in surface to volume ratio. In the present work, continuous film (low surface area) and electrospun nanofibre mats (high surface area) are used as interleaves to toughen carbon/epoxy laminates. The dissolution behaviour of phenoxy fibres in epoxy resins at different isothermal conditions was examined as a model study, while the interlaminar toughening effect and mechanism is discussed for both interleaf systems.

2. Experimental

2.1. Materials and sample preparation

2.1.1. Materials

Polyhydroxy ether bisphenol A (phenoxy) was supplied by InChem (PKHH) with an average molecular weight (M_w) of 52,000, and a glass transition temperature (T_g) of 92 °C. The composite system employed consists of high strength 2×2 twill carbon fibre fabrics, with an areal weight of 286 g/m², and RTM6-2 which is a two components aerospace grade epoxy, both from Hexcel. After mixing this two component system, the formulation of the RTM6-2 is similar to RTM6, consisting of tetraglycidyl diamino-diphenyl-methane (TGDDM) and diamino-diphenyl sulphone (DDS). The PTFE copolymer release film with a thickness of 12 μm (A6000®) was supplied by Aerovac Systems Ltd. The mould release agent was purchased from Frekote, and an adhesive spray was purchased from 3M. For the solution-based electrospinning of nanofiber mats, Chloroform and N,N-Dimethylformamide (DMF) was purchased from Fisher Scientific and Sigma–Aldrich, respectively.

2.1.2. Sample preparation

For the phenoxy dissolution experiments, melt-extrusion and electrospinning was used to produce phenoxy fibres with diameters ranging from a few hundred nm to 200 μm, hence possessing different surface areas. For the electrospun fibre mats, phenoxy pellets (15 wt.%) were dissolved in a mixture of chloroform and DMF (80/20 by weight) with optimized processing conditions of 1 ml/h feeding rate, 20 cm of collector distance, and 24 kV voltage after various trials. Produced porous nanofibre mats with an average fibre diameter of 700 nm were peeled off from a substrate and used as interleaves, with thicknesses ranging from 35 to 150 μm. Continuous phenoxy films with thicknesses ranging from 6 to 60 μm were produced via a simple solution based bar-coating method. The surface area of these electrospun fibre mats varied from 9.1×10^{-1} to 8.2×10^{0} m² and was estimated from their average diameter and measured weight.

For the manufacturing of composite laminates, a steel plate was used as a base to create a resin infusion mould. This plate was cleaned first with acetone, and subsequently treated three times with mould release agent. Tacky tape was used to create the mould, with inlet and outlet tubes placed at both ends of the mould to facilitate resin flow. Fabrics of desired dimensions were placed into the mould, with a PTFE release film (12 μm) embedded at the mid-plane to facilitate crack initiation (see Fig. 1). Peel-ply was placed on top of the fabrics while a flow media was applied on top of the peel-ply to facilitate resin flow.

In the case of interleaved specimens, the thermoplastic interleaf in the form of film or fibre mat was placed in between the 5th and 6th ply of carbon fabric. The thicknesses of all produced laminates are within testing standard requirements. A typical curing cycle involved heating at a rate of 3 °C/min from room temperature to 140 °C for 1.5 h, followed by a post cure at 180 °C for another 2 h. Specimen cutting and preparation is same as described in our previous studies [43].

2.2. Characterization

2.2.1. Optical microscopy

Optical microscopy (Olympus BX60F) was used to examine the morphology of the electrospun fibres. Electrospun fibres with different diameters were collected on glass slides and observed under an optical microscope equipped with a digital camera.

To study the dissolution behaviour of phenoxy fibre in epoxy resin, a Linkam HFS600 heating stage was fitted to an Olympus BX60 optical microscope. The temperature of the heating stage was controlled by LinkSys32 software, while optical microscopy images were processed using Image-Pro Express software. Phenoxy fibres (with diameters ranging from 1 μm to 200 μm) were placed on a glass slide and positioned under the optical microscope, with both heating stage and epoxy resin pre-heated to 80 °C before a droplet of epoxy (RTM6-2) was placed on the glass slide. A thin glass cover slide was then positioned on top of the epoxy droplet before observation. The same procedure was used for temperatures of 90 °C and 100 °C, as well as different fibre diameters (1–200 μm).

2.2.2. Mode-I interlaminar fracture toughness testing (DCB)

Double cantilever beam (DCB) tests were performed for Mode-I interlaminar fracture toughness characterization, in accordance with ASTM D5528 [44]. Detailed test procedures and data interpretation can be found elsewhere [43].

2.2.3. Fractography

The fracture surface of the tested specimen was examined under scanning electron microscopy (SEM) (FEI Inspect-F). Images at different magnifications were taken with the aim to obtain some insight in potential toughening mechanisms.