METAL TRIFLATES AS CATALYTIC CURING AGENTS IN SELF-HEALING FIBRE REINFORCED POLYMER COMPOSITE MATERIALS

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ABSTRACT

High performance, damage tolerant fibre reinforced polymer (FRP) composite materials are currently required to demonstrate no propagation of any sub-surface structural micro-cracking when under service load, thereby encouraging overdesign and limiting the inherent lightweight nature of such a material. By incorporating self-healing functionalities, in-situ autonomous repair can be initiated in the event of damage to maintain structural integrity while ultimately realising lighter and more sustainable structures. We have demonstrated metal triflate initiated ring opening polymerisation (ROP) of epoxide resin [1] in FRPs to restore >99% of the host matrix fracture toughness after damage under Mode I tests.

Optimising the polymer composition via differential scanning calorimetry (DSC) identified the key parameters to achieve autonomous curing under ambient conditions. Initial and self-healed performance was evaluated using FRP E-glass double cantilever beam (DCB) coupon mechanical test specimens with embedded microvascular channels for self-healing agent delivery. Full recovery of fracture toughness (>99%) was demonstrated while achieving the following requirements: low cost, low toxicity, autonomous curing, autonomous delivery, usability, manufacturing processability and applicability to existing aerospace and automotive maintenance programs.

Brittle and ductile cohesive failure mechanisms resulted from inclusion of a solvent (ethyl phenylacetate) within the healing agent under low (10 wt%) and medium (25 wt%) concentrations. Therefore, the failure mechanism can be adapted as the solvent acts as a plasticiser in the self-healing agent. This was further confirmed by imaging fracture plane surfaces via scanning electron microscopy (SEM). The adhesive repair was typically ~100 μm in thickness, comparable to damage voids present in impact damaged FRP composite materials.

1. INTRODUCTION

Micro-cracking in FRP materials can ultimately lead to catastrophic failure by rapid propagation throughout the laminated structure. For example, this damage can occur between stacked laminae, manifest itself as fibre-resin interfacial debonding or arise from manufacturing defects, causing stress concentrations which lead to the onset of premature component failure. In this research the focus has been on the implementation of previously developed self-healing agents (SHAs) by Coope et al., [1] to achieve a self-healing FRP material using typical industrial composite manufacturing techniques.

2. MATERIALS

Solid-state, metal triflate, catalysts stable to air and moisture were used as curing agents for the polymerisation of an oligomeric diglycidyl ether bisphenol A (EPON 828) epoxy resin. Two catalysts, scandium(III) triflate (Sc) and aluminium(III) triflate (Al) were considered. Polymer formulations containing 10 wt% (E10) and 25 wt% (E25) of a non-toxic solvent, ethyl phenylacetate (EPA) (added to reduce viscosity), were investigated for their effect on mechanical performance recovery. The thermal reactivity of these materials were evaluation using differential scanning calorimetry (DSC), a TA Instruments Q200 DSC was used to study non-isothermal curing via dynamic scans. Samples were heated from 0 to 250 °C at a heating rate of 10 °C/min under a flow rate of 50 mL/min of nitrogen as the purge gas.

E-glass/epoxy (Hexply 913, Hexcel Composites) unidirectional (UD) plates (300 mm x 220 mm x 3.8 mm) were manufactured using hand lay-up (28 ply). Cure was undertaken according to the manufacturer's recommendations of 125 °C for 1 hour and a pressure of 700 kPa. Stainless steel wire (ca. 0.5 mm in diameter) pre-coated with PTFE release agent was placed parallel to the fibre direction in pre-cut 0.5 mm channels (equal to the thickness of 4 plies) centred on the mid-plane. Release film (15 µm thickness) was placed from the laminate edge to 25 mm before the start of the vascules. Cured composite plates were cut into DCB coupon specimens using a water-cooled diamond grit saw (195 mm x 20 mm x 3.8 mm). Piano hinges were bonded in place using Hexcel Redux 810 adhesive onto grit-blasted surfaces as preparation for mechanical testing.

3. METHODS

An Instron 3343 fitted with a 1kN load cell was used to initiate and propagate Mode I crack opening. Double cantilever beam (DCB) E-glass composite test specimens fixed via attached piano hinges were loaded at a displacement rate of 2 mm/min in accordance with ASTM 5528-01 [2, 3]. Cracks were propagated for 75 mm from the point of initiation and crack length recorded with a video camera.

Specimens were healed after initial fracture using the prescribed healing agent, delivery method and cure temperature (Table 1). SHAs were delivered via the edge-located vascules using 26 gauge hypodermic needles. Healed specimens were re-tested as outlined above for initial fracture.

4. RESULTS

The results revealed the two achievable resultant failure mechanisms, ductile and brittle, by incorporating EPA solvent at certain prescribed loadings. Therefore, self-healed specimens containing 25 wt% EPA with respect to EPON 828 failed in a way that is comparable to the initial composite fracture under Mode I testing. Equally, curing temperature variance (45 °C, 80 °C and ambient temperature) maintained this failure methodology, with higher healing efficiencies being achieved for samples healed at higher temperatures and/or with a higher catalyst loading (Figure 1).

Table 1. Specimen derivatives used to demonstrate self-healing performance.

Designation	Monomer Solution[a)]	Catalyst	Catalyst Loading [pph][b)]	Healing Temperature [°C]		
				45	80	RT
E10 Sc (M)	E10	$Sc(OTf)_3$	3.125 (M)	X	X	X
E10 Al (M)		$Al(OTf)_3$	3.125 (M)	X		
E25 Sc (M)	E25	$Sc(OTf)_3$	3.125 (M)	X	X	X
E25 Sc (H)			6.25 (H)	X		X
E25 Sc (L)			1.5625 (L)	X		
AUTO E25 Sc (M)			3.125 (M)	X		
E25 Al (M)		$Al(OTf)_3$	3.125 (M)	X		
E25 DETA		DETA	12			X

a) **E10**: 90 wt% EPON 828, 10 wt% Ethyl phenylacetate (EPA); **E25**: 75 wt% EPON 828, 25 wt% EPA. b) (L) = low loading, (M) = medium loading, (H) = high loading

A 26% minimum healing efficiency increase was observed for implementing these SHAs compared with the commercial-based EPON 828/DETA system (Figure 1). E25 Sc healed test specimens achieved a minimum healing efficiency of 129% via the injection of a pre-mixed solution at 45 °C, demonstrating full recovery of fracture toughness. Ultimately, autonomous curing was one of the main objectives for this self-healing system. Thus, curing at ambient temperature provided a minimum healing efficiency of 113% for this same system. A modest increase of 30% healing efficiency resulted from healing at 80 °C when compared with healing at low temperature. The highest healing efficiency was achieved by introducing a higher catalyst concentration to E25 Sc cured at 45 °C. This resulted in a 176% load recovery and a 352% fracture toughness recovery. Furthermore, an autonomous delivery method facilitated by infusion of separate $Sc(OTf)_3$-EPA and EPON 828 solutions via parallel vascules achieved a 100% load recovery and 88% fracture toughness.

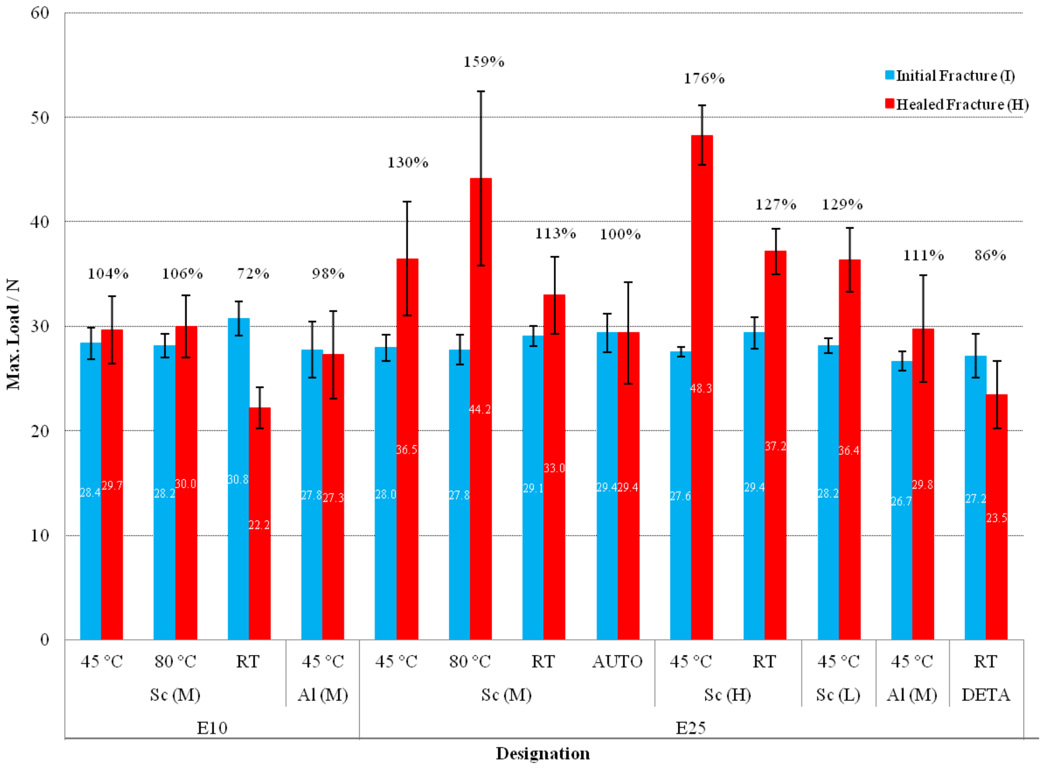

Figure 1: Healing performance for maximum load

5. CONCLUSIONS

Evaluation of self-healing agents using a fibre-reinforced polymer (FRP) double cantilever beam (DCB) geometry demonstrated full recovery of material properties under Mode I test. A cohesive failure of self-healed polymer, containing variable solvent concentrations, resulted in either a brittle or ductile fracture mechanism. This research further demonstrates the applicability and tailorability of the underpinning chemistry in this self-healing system and how it is not limited by the delivery mechanism (i.e. microcapsules, hollow glass fibres (HGF) or microvascular channels) or the end-user application.

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