Composites Science and Technology 72 (2012) 453–460

Contents lists available at SciVerse ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Thermally activated healing in a mendable resin using a non woven EMAA fabric

Russell J. Varley [a,*], Grace P. Parn [b]

[a] CSIRO Materials Science and Engineering, Private Bag 33, Clayton South MDC, Victoria 3169, Australia
[b] School of Aerospace, Mechanical and Manufacturing Engineering, RMIT University, Melbourne, Australia

ARTICLE INFO

Article history:
Received 14 June 2011
Received in revised form 26 November 2011
Accepted 3 December 2011
Available online 9 December 2011

Keywords:
A. Smart materials
B. Fracture toughness
B. Impact behaviour
Self healing

ABSTRACT

This paper explores the efficacy of polyethylene-*co*-ethacrylic acid (EMAA), as a thermally activated thermoplastic healing agent embedded within a carbon fibre reinforced epoxy composite. EMAA fibres have been shown to effectively restore mode I properties in a fibre reinforced composite after thermal activation yet other forms of the healing agent or modes of deformation have so far not been studied at all. This work, uses EMAA in the form of a non-woven mesh, rather than a woven fabric to study the healing mechanism and effectiveness of property restoration for mode I (crack opening) and mode II (shear) failure as well as for high speed impact. Property restoration after mode I damage was found to be over 200% and increased with increasing EMAA concentration. For mode II shear failure, the property restoration was reduced to a little over 100% regardless of EMAA concentration. Mode II analysis also showed that the modulus could be restored to about 80% of its original value when modified with EMAA. Repeated impacting using a falling weight test produced no property restoration after healing, yet the modified laminates appeared protected from further damage compared with an unmodified laminate. This was attributed to the formation of a ductile thermoplastic layer mitigating further damage. Scanning electron microscopy revealed that regardless of the extent of healing, the form of the healing agent or the mode of damage, the unique pressure delivery mechanism previously identified, was always observed to occur.

1. Introduction

An engineering material with the ability to restore its properties subsequent to a damage event is clearly of great value in structural applications where repair is difficult or impractical in the case of complex componentry or where the material is subjected to extreme environments. New materials such as these, with increased service lifetimes and reduced maintenance regimens will furthermore play an important role in fostering a sustainable usage of energy and resources. The development of self healing materials therefore is a response to this challenge and has already spawned a variety of approaches which have been extensively reviewed [1–5]. Thermoplastic modifiers as healing agents for composite materials are one such strategy that has several advantages compared with the more common micro-encapsulation approach. These modifiers are simple to implement, repeatable over a number of damage events and can be indefinitely stable until required. However, the fundamental challenge to this intrinsic healing approach is that the thermoplastic must be stable during fabrication yet still able to be activated externally afterwards.

Although the work of Zako and Takano [6] is the first reported application of thermoplastic modifiers as healing agents in composite materials, Wool and O'Connor were the first to propose a theory of crack healing in thermoplastic polymers [7]. For any thermoplastic healing approach they suggested that the following five stages are necessary: surface re-arrangement, surface approach, wetting, diffusion and randomisation. Zako and Takano illustrated some of these mechanisms by showing that 50 μm sized thermosetting epoxy particles embedded in an epoxy resin matrix, could melt and flow into delaminated regions and restore flexural and tensile fatigue properties after thermal activation. In addition to the healing mechanism it was critical that the composite was processed below the melting point of the epoxy healing agent, so that during subsequent thermal treatment the embedded adhesive was still able to function as a healing agent. The strategy used by Hayes et al. [8,9] is similar in that healing is activated by heating the composite above the melting point of the healing agent but the inherent miscibility and subsequent mobility of the thermoplastic in an epoxy network is what underpins the healing mechanism. The chain diffusion and entanglement processes across the crack plane means that this mechanism is ideal for healing prior to significant crack opening. Other strategies however are emerging, such as using thermoplastic oligomers containing reversible covalent bonds via a Diels Alder mechanism [10], with the capacity to depolymerise and flow into a damage zone aided by solvent swelling. Recent work by Luo et al. [11], takes advantage of the volume expansion of the polycaprolactone (PCL) thermoplastic above

* Corresponding author.
E-mail address: russell.varley@csiro.au (R.J. Varley).

0266-3538/$ - see front matter Crown Copyright © 2011 Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.compscitech.2011.12.007

its melting point to heal an epoxy/PCL matrix blend. In this way, the PCL is seen to bleed into a cavity and has been shown to produce greater than 100% healing as determined from fracture toughness measurements. Meure et al. [12–14] also developed a novel mendable composite system using a poly(ethylene-*co*-methacrylic acid) (EMAA) thermoplastic modifier in an epoxy matrix. The healing mechanism originates in this case from chemical reactions between the carboxylic acid groups in the thermoplastic occurring during cure of the epoxy resin producing volatiles which are trapped in the thermoplastic until activated. When heated above 100 °C, the volatiles expand greatly and pushing the melted healing agent into the crack plane of a damage zone. As the temperature returns to ambient conditions the EMAA further binds the two fracture surfaces together through a hydrogen bonding mechanism and van der Waals forces. Healing efficiencies of over 100% were achieved according to mode I fracture toughness when the unique pressure delivery mechanism was activated.

Previous work has shown excellent property restoration after healing according to mode I failure and when the EMAA is in the form of a 90° woven fabric. This work therefore, continues to explore the robustness of this mechanism with respect to different modes of deformation and the form of the healing agent. Instead of using a woven fabric as per previous work [14], a non-woven mesh of varying areal densities has been used, imitating successful interlayer toughening strategies [15–20] and examining its potential application to a manufacturing environment. The healing mechanism has been evaluated using mode I (crack opening) and mode II failure (shear) as well as repeated impact damage using a high speed falling weight. Scanning electron and optical microscopy has been used to confirm the healing mechanism.

Table 1
Areal density of EMAA layers.

Number of layers	Areal density (g/m^2)
1	55.06
2	110.12
3	165.18

2. Experimental

2.1. Materials

Carbon fibre laminates were prepared using diglycidyl ether of bis-phenol A, (DGEBA, DER-331, Dow Plastics, Australia) and triethylenetetramine (TETA, DEH-24, Dow Plastics Australia). The carbon fibre used was a SigmaTex 199 gsm plain weave 3 k tow (Lavendar Racing, Australia). The healing agent, EMAA (Nucrel 2940, DuPont Packaging and Industrial Polymers) was used in the form of a non-woven mesh of EMAA fibres drawn from a Haake Minilab extruder set at 20 Ncm and 140 °C with winding speeds of 160 m/min and 400 m/min to produce 50–75 μm diameter fibres. These fibres were then arranged into a loose unwoven mesh, which was strengthened using a hot press at 80 °C for 10 min with sufficient pressure to consolidate the fibres. This mesh was then cleaned by soaking it in ethanol to remove the processing oil and other impurities. Fig. 1 illustrates the processing sequence of EMAA, beginning as an extremely fragile non-woven mesh, to the strengthened mesh after thermal treatment and finally as it is applied to a carbon fibre surface.

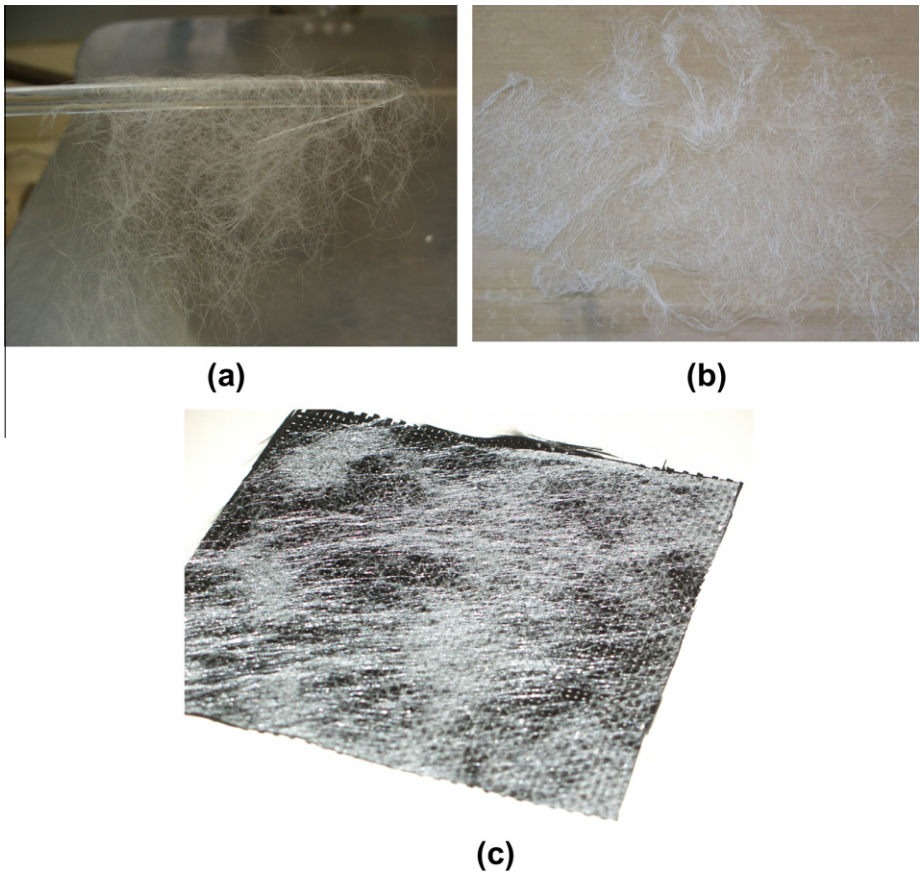

Fig. 1. EMAA non-woven mesh, (a) prior to any processing, highlighting the fragile form. (b) EMAA after thermal processing to enhance structural integrity but prior to washing. (c) EMAA after pressing and consolidation onto a carbon fibre sheet.