Composites: Part A 43 (2012) 512–518

Contents lists available at SciVerse ScienceDirect

Composites: Part A

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

Interlayer self-healing and toughening of carbon fibre/epoxy composites using copolymer films

Chun H. Wang [a,*], Komal Sidhu [a], Tao Yang [a], Jin Zhang [a], Robert Shanks [b]

[a] Sir Lawrence Wackett Aerospace Research Centre, School of Aerospace, Mechanical and Manufacturing Engineering, RMIT University, GPO Box 2476, Melbourne, VIC 3001, Australia
[b] School of Applied Sciences, RMIT University, GPO Box 2476, Melbourne, VIC 3001, Australia

ARTICLE INFO

Article history:
Received 10 May 2011
Received in revised form 22 October 2011
Accepted 26 November 2011
Available online 3 December 2011

Keywords:
A. Polymer matrix composites (PMCs)
B. Fracture toughness
C. Damage mechanics
D. Fractography

ABSTRACT

This paper presents an investigation of the combined self-healing and toughening performance of two copolymers: thermoplastic poly(ethylene-*co*-methyl acrylate) (EMA) and poly(ethylene-*co*-methacrylic acid) (EMAA). Carbon fibre composites were manufactured from unidirectional prepregs with rectangular-shaped patches being placed between composite plies. Results from double-cantilever-beam and short-beam-shear testing show that the incorporation of mendable polymers improves interlaminar fracture toughness but causes a reduction in interlaminar shear strength. The healing efficiency in terms of restoration of the interlaminate fracture energy scales linearly with the areal percentage of self-healing material. Microstructure study revealed distinct difference in the fracture surfaces of composites with EMA and EMAA, with EMA displaying extensive nano-scale porous structures in contrast to the more homogenous single phase structure from EMAA.

1. Introduction

Structural polymers and polymer matrix composites are susceptible to matrix cracking and delamination, either due to service induced mechanical and thermal loading, or due to foreign object impact. Once cracks are formed, the mechanical performance and structure integrity of the composite material systems degrade, which can lead to catastrophic failure. The problem of matrix cracking and delamination of composites poses a significant economic burden of costly inspections and repairs. In response to this challenge, self healing techniques have been developed to effectively extend the life-span of polymer-based materials and structures, bringing direct benefits to economic and human safety attributes [1,2]. A variety of methods has been utilised to recover the mechanical properties of thermoset polymers and composite structures [3], including the hollow fibre approach [4–6], the microencapsulation approach [7–9], use of thermally reversible bond formation [10,11], inclusion of thermoplastic additives [12,13], metal-ion-mediated healing [14,15], etc. Among these technologies, the thermally reversible healing agents offer certain advantages over other techniques, because they not only eliminate the need for adding catalyst or monomer that is necessary for the microencapsulation approach, they have the capability of multiple crack healing at the same location since the healing agent is not consumed during the repair process [16,17]. Another significant benefit is that thermoplastics can improve the fracture toughness of thermoset composites. However, the healing mechanism of thermoplastics does require external intervention, e.g., the application of heat.

Ionomers have existed since the 1960s, however, their self-healing behaviour has only been recently studied. Thermoplastic poly(ethylene-*co*-methyl acrylate) (EMA) and poly(ethylene-*co*-methacrylic acid) (EMAA), the latter being partially neutralized by metal ions, have demonstrated the unique ability to successfully repair damage of different types, in particular, the damage from a ballistic impact [18,19]. Infrared studies by Blyler and Hass [20] and MacKnight et al. [21] showed that hydrogen bonding existed above the melting temperature of EMAA. So when these ionomer films are heated above their melting temperature, e.g., due to ballistic impact, an instant and automatic puncture reversal has been observed with only a scar remaining at the healed site [19,22,23]. Kalista et al. [18] observed that interfacial welding can occur below the melting temperature, although higher temperatures may produce better healing due to increased self-adhesion and chain mobility. Although several hypotheses have been put forward to explain how this has happened, including the order–disorder transition of the ionic content upon heating and cooling [24], the electrostatic attractive forces derived from the electrically bound physical clusters [25], combined with the melt flow behaviour of these copolymers, the precise healing mechanism of ionomers remains not well understood.

Copolymers, such as EMAA, without the addition of metal ions, have also been investigated for their self-healing efficiency, either as dispersed particles in the matrix resin [26] or as filaments in-

* Corresponding author. Tel.: +61 3 99256115; fax: +61 3 9925 6108.
E-mail address: chun.wang@rmit.edu.au (C.H. Wang).

1359-835X/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.compositesa.2011.11.020

serted between carbon–epoxy laminas [27], attributing to their relatively good processability. EMAA is an adhesion promoter with high peel resistance but poor shear strength, due to the high elongation of these polymers. For example, the shear and tensile strengths of EMAA at room temperature have been reported to be close to 8.6 MPa [28] and 16 MPa [32], respectively, much lower than epoxy-based structural adhesives at room temperature.

Apart from the low shear and tensile strength of copolymers, such as EMAA, another major issue with the use low melting temperature thermoplastics as self-healing agents is their limited melt flow during healing, primarily due to the high viscosity of these materials even at temperatures well above their melting temperatures. Meure et al. [26,27] reported that the expansion of EMAA, assisted by bubble expansion during healing [26], tended to achieve a surface coverage around 50%. Furthermore, the EMAA polymer tends to travel along EMAA fibres, with limited lateral expansion [27]. Consequently the self-healing agents, either in particle or fibre form, may only partially cover the fractured surface unless an extremely large amount of self-healing agents are employed. Since the low melting EMAA and EMA have much lower shear strengths than the interlaminar strength of carbon–epoxy laminates, any increase in the content of healing agent will be accompanied by a reduction in the interlaminar shear strength of the composite laminates. Therefore, it is desirable to keep the use of thermoplastic healing material to the minimum to ensure that the incorporation of self-healing functionality does not substantially weaken the composites [29]. In this context, it is important to investigate the effect of partial coverage on the performance of self-healing, given that the healing efficiency depends on the areal coverage by the healing agents.

The aim of the present research is to investigate the effect of incomplete surface coverage on the self-healing performance by thermoplastics. Small EMA and EMAA rectangular sheets were inserted between carbon–epoxy prepreg plies prior to manufacture of the composites. Mode I interlaminar fracture toughness and short beam shear tests were performed to examine the healing efficiency of the composite laminates. The fracture surface of the healed double cantilever beam (DCB) specimens and the cross-section of the healed short beam shear (SBS) specimens were examined by scanning electron microscopy (SEM) in comparison with the un-modified specimens that did not contain any healing agent.

2. Experimental methods

Both EMA and EMAA were obtained in pellet form from Aldrich Chemical Company, Inc. The pellets were converted into thin sheets of an average thickness of 0.15 mm by hot pressing at 140 °C. Four different rectangular sheets with dimensions including 6 mm × 6 mm, 8 mm × 8 mm, 10 mm × 10 mm, and 10 mm × 14 mm were cut for insertion between carbon–epoxy prepreg layers. A VTM 264 prepreg (Advanced Composites Group) was used for composite fabrication. A total of five thin patches were placed over an area of 20 mm × 70 mm, as schematically shown in Fig. 1a. This gives rise to areal percentages of 12.8%, 22.8%, 35.7%, and 50%. Since the density of EMAA is approximately 0.93 g/cm^3, the area density of 23% is equivalent to a content of 35 g/m^2. Meure et al. [27] reported that at this content, the incorporation of EMAA, either in particle form or fibre form, could fully recover mode I fracture toughness. Healing agents were inserted in the middle five layers of the DCB laminate and between every layer of the SBS laminate. A lay-up scheme of $[0]_{16}$ was used and the composite laminates were cured in an autoclave at 75 °C for 5 h with N_2 pressure of 830 kPa followed with a post cure at 150 °C for 1 h in an oven. A composite laminate without healing agents was used for comparison.

Composite specimens with the dimensions of 120 mm × 20 mm × 3.6–4.0 mm were prepared for DCB testing, referring to Fig. 1b, and composite specimens with the dimensions of 25 mm × 10 mm × 3.6–4.2 mm were used for SBS testing. The DCB and SBS tests were performed in accordance with the ASTM D5528 standard and the ASTM D2344 standard, respectively. Teflon films were used as crack initiators for the fracture toughness tests. The DCB specimens were unloaded when the crack propagated to near the end of the specimen, while the SBS specimens were unloaded once the load had decreased by more than 30%. Healing was activated at 150 °C for a period of 30 min. After healing, the coupons were re-tested to assess the repair efficiency. SEM observations of the fractured specimens from both the un-modified (laminate without any healing agent) and the healed composites were made to examine the healing and toughening mechanism by interlayer copolymers. Gold coating was applied to the SEM specimens before imaging.

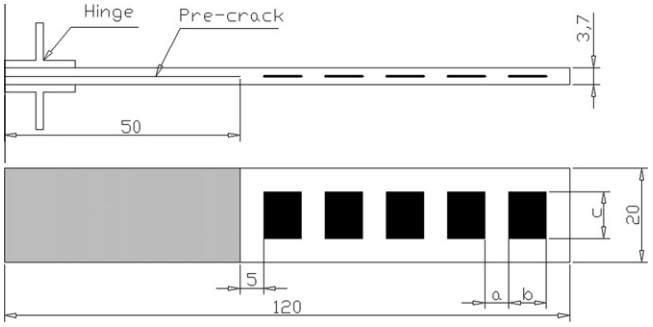

Fig. 1. Configurations of (a) self-healing patches embedded in composite laminate and (b) double-cantilever beam specimen showing dimensions.

3. Results and discussion

Typical load vs. crack opening displacement (COD) curves for DCB tests for laminates containing 23% EMA and EMAA are presented in Fig. 2. For both the un-modified and mendable composite DCB specimens, the applied load increased linearly initially, followed by gradual load drops as the crack propagated. It is

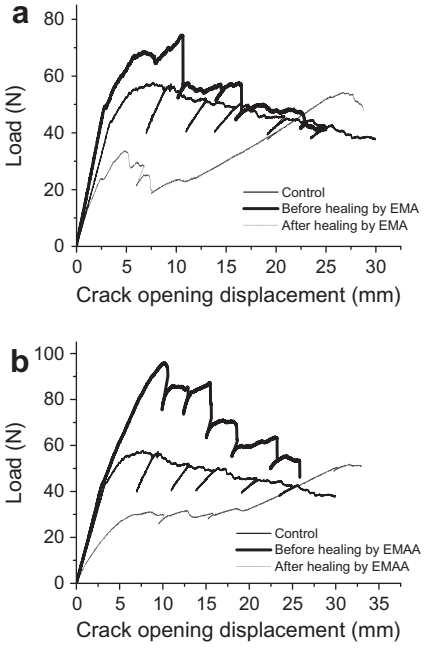

Fig. 2. Load vs. crack opening displacement (COD) curves from DCB tests affected by healing agents (a) EMA and (b) EMAA.