

An efficient healing agent for high temperature epoxy composites based upon tetra-glycidyl diamino diphenyl methane



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ABSTRACT

Poly(ethylene-co-methacrylic acid) (EMAA) as a thermally activated healing agent in a high performance, high temperature tetra-glycidyl methylene dianiline (TGDDM)/diethyl toluene diamine (DETDA) mendable epoxy composite is reported for the first time. Despite curing above EMAAs melting point ($T_m = 85\text{ }^\circ\text{C}$), healing occurred by incorporating a preliminary low temperature curing step of 5 h at $80\text{ }^\circ\text{C}$, prior to cure at $177\text{ }^\circ\text{C}$. Healing occurred via the pressure delivery mechanism derived from tertiary amine catalysed surface condensation reactions between EMAA and hydroxyl groups from the epoxy resin. Healing efficiencies of 36%, 55% and 105% were achieved after heating at $150\text{ }^\circ\text{C}$, $200\text{ }^\circ\text{C}$ and $230\text{ }^\circ\text{C}$ respectively, but decreased rapidly with continued healing. Healing at $150\text{ }^\circ\text{C}$ and $200\text{ }^\circ\text{C}$ revealed significant healing despite remaining in the glassy state. In addition, EMAA enhanced mode I interlaminar fracture toughness by more than 270% for both the DETDA and 4,4-DDS networks.

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1. Introduction

Mendable polymers are an emerging family of resins that when damaged can be repaired simply and conveniently through the application of heat, irradiation or some other external stimuli [1–4]. When activated, a reversible chemical reaction or physical process forms new bonds that restore somewhat the properties of the damaged polymer. Although not self-healing in an automatic sense, mendable resins have several advantages compared with other self-healing technologies including high efficiency, repeatability and dormancy. As such, they are particularly useful when applied in composites that are susceptible to delamination and matrix cracking.

Many strategies have been used to develop this type of intrinsic healing for polymers, with thermoplastic modification being one particularly simple, convenient and effective approach. Early work by Zako and Takano [5,6], used epoxy thermosetting particles as healing agents in an epoxy matrix and achieved excellent recovery to the stiffness and fatigue properties of a neat epoxy network and polymer composite after thermal activation. The mechanism was attributed to the two-phase microstructure containing small active particles (less than $50\text{ }\mu\text{m}$) dispersed in an epoxy matrix that

melted and flowed into a damaged region. A different approach by Jones et al. [7,8] used a miscible thermoplastic agent that attached to the epoxy network via non-covalent hydrogen bonding. When heated, the thermoplastic was released to migrate across the crack interface and heal the damaged network. Restoration of the impact strength of a fibre reinforced epoxy composite was achieved for multiple damage events at a concentration of 7.5 wt% thermoplastic, indicating there was an optimum microstructure for healing. Other approaches have used shape memory alloys [9], co-continuous morphologies in thermosetting/thermoplastic blends [10] and other thermoplastic agents that simply exhibit a particularly low viscosity during healing [11].

Poly(ethylene-co-methacrylic acid) (EMAA) is another effective thermoplastic healing agent when used as a two-phase additive in various forms, sizes and compositions [12–14] for the room temperature cured diglycidyl ether of bisphenol A (DGEBA) and triethylene tetramine (TETA) resin systems [15–18]. The healing mechanism originates from a condensation reaction between hydroxyl groups of the epoxy/amine network formed during cure and the carboxylic acid groups of EMAA, as shown in Fig. 1. This reaction however, is dependent upon tertiary amine catalysis, which itself is only formed as the resin cures, emphasising the role of cure conversion and epoxy/amine reactivity in controlling the healing process. Water formed as a by-product of the condensation reaction at the interface subsequently coalesces into a bubble

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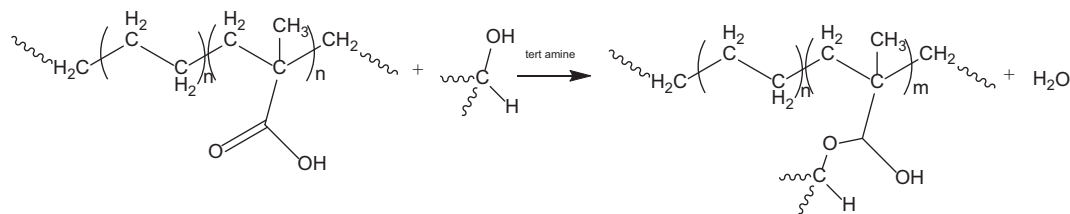


Fig. 1. Tertiary amine catalyzed condensation reaction providing the origin of the self-healing mechanism.

embedded within the EMAA thermoplastic and remains dormant until activated by heat [16]. Heating at 150 °C, well above the melting point of the EMAA ($T_m = 85$ °C), expands the bubble greatly, pushing the molten thermoplastic into a cavity or damaged region subsequently binding the fracture surfaces together upon cooling. Hence the term, pressure delivery is used to describe the mechanism because the build-up of internal pressure within the bubble delivers the molten healing agent to a damage zone.

While exhibiting high healing efficiencies for the room temperature cured DGEBA/TETA resin [15,17], the low melting point of EMAA has limited the scope of epoxy/amine resin systems evaluated because of the perceived need to ensure that EMAA remains solid and immiscible during the entire cure regime. High temperature, high performance epoxy resin systems however, require high cure temperatures, well above the melting point of the EMAA to fully realise their properties. Unfortunately, EMAA appeared to degrade when cured directly at high temperature in a DGEBA/diethylene toluene diamine (DETDA) resin system [19] and produced no healing at all. Clearly, another approach is required if EMAA is able to be used for high temperature resin systems. Infrared spectroscopic studies by Meure et al. [20] reveal non-covalent attachment of the epoxide and amino groups to the EMAA occurs via hydrogen bonding and ionic associations respectively, at temperatures just below the melting point of the EMAA. When the temperature was increased to above the melting point of the EMAA, surface bubbles were still observed indicative of the occurrence of the condensation reaction. This showed that this reaction, critical to healing, could still occur despite the concurrent melting of the EMAA. It is proposed therefore, that in this case, encouraging non-covalent attachment of epoxide or amino groups to EMAA at low temperature initially, could be a novel route to inhibit degradation, facilitate the condensation reaction during cure at high temperature and thus enable healing.

To explore this hypothesis, an EMAA modified and unmodified tetra functional epoxy resin tetra glycidyl methylene dianiline (TGDDM) was cured separately with two aromatic amine harden-

ers, DETDA and 4,4 diamino diphenyl sulphone (4,4-DDS), known for their high performance, high temperature applications. Two cure profiles were used, the first consisting of a single step of 8 h at 177 °C, while the second included a preliminary initial step of 5 h at 80 °C followed by 8 h at 177 °C. Healing efficiency, temperature and repeatability, as well as fracture toughness enhancement of the EMAA modified composites were investigated using dual cantilever beam testing (DCB). Rheological curing studies were performed to understand the changes in viscosity during cure, and dynamic mechanical thermal analysis (DMTA) was used to choose the most appropriate healing temperatures. The healing mechanism was investigated using scanning electron microscopy (SEM) and near infra-red (NIR) spectroscopy. A companion study exploring similar concepts, using diglycidyl ether of bisphenol A (DGEBA) as a high performance epoxy matrix is recommended for comparing the impact of crosslink density on healing efficiency [21].

2. Experimental

2.1. Materials

The epoxy resin used in this work was tetraglycidyl diamino diphenyl methane (TGDDM, MY721, EEW = 116) obtained from Vantico, Australia. Prior to use, the epoxy resin was degassed in a vacuum oven at 90 °C. The aromatic amines used were diethyl toluene diamine (DETDA, Albermarle, USA) and 4,4 diamino diphenyl sulphone (4,4-DDS, Vantico, Australia) and were used as received. The solid BF_3 methyl amine adduct catalyst was obtained from Sigma-Aldrich (Australia). The thermoplastic healing agent poly(ethylene-co-methacrylic acid) (EMAA, Nucrel 2940, DuPont Polymers, USA) was received as pellets then cryogenically ground and sieved into particle sizes between 295 μm and 495 μm and dried in a vacuum oven at 60 °C. The chemical structures are shown in Fig. 2.

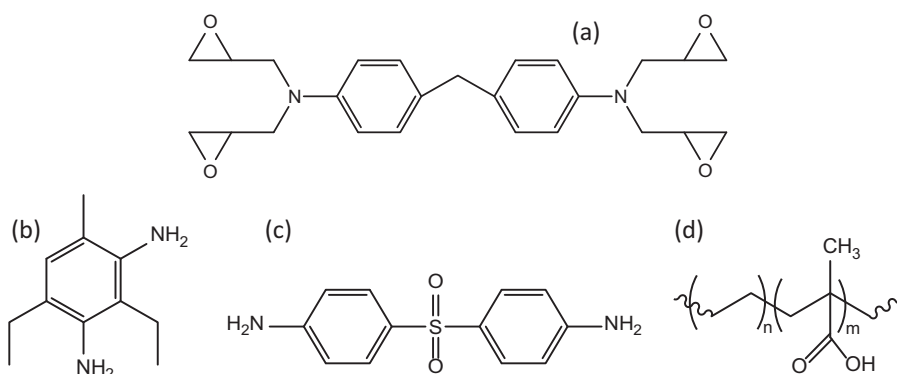


Fig. 2. Molecular structures of the chemicals used in this work. (a) The epoxy resin was tetra glycidyl diamino diphenyl methane (TGDDM) of bisphenol A ($n = 0.17$). The amine hardener was (b) diethyl toluene diamine (DETDA) and (c) 4,4 diamino diphenyl sulphone (4,4-DDS). The poly(ethylene-co-methacrylic acid) thermoplastic healing agent is shown in (d).

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